Peculiarities of thermo-morphologic and thermotropic transformations of heterophase regions: nematic ↔ isotropic phase transition in 4-n-Alkyl-4'-cyanobiphenyl mesogens

ATILLA EREN MAMUK, ARIF NESRULLAJEV*

Mugla Sitki Koçman University, Faculty of Natural Sciences, Department of Physics, Laboratory of Liquid and Solid Crystals, 48000 Mugla Kotekli, Turkey

Important peculiarity of phase transitions in liquid crystalline materials is availability of the heterophase regions, in which low temperature and high temperature phases simultaneously take place. In this work, peculiarities of the the thermo-morphologic and thermotropic transformations of the heterophase regions of phase transitions between nematic mesophase and isotropic liquid vs. boundary conditions have been investigated. 4-n-alkyl-4'-cyanobiphenyl liquid crystals with different length of the alkyl chain were objects of our investigations. Effect of thickness of liquid crystalline layer in the sandwich-cells on the thermo-morphologic and thermotropic properties of liquid crystals under investigations has been observed. Temperature and linear widths of the heterophase regions of phase transitions were determined with high accuracy. Change of the temperature and linear widths of the heterophase regions as function of thickness of liquid crystalline layer was found.

1. Introduction

Liquid crystals are important materials in soft matter and in definite temperature interval exhibit rheological properties as liquids and physical anisotropic properties as solids. Important peculiarities of liquid crystalline materials are availability of various phase transitions between various liquid crystalline mesophases and between liquid crystalline mesophases and isotropic liquid. These phase transitions are sufficiently sensitive to different external influences e.g. the electric, magnetic and thermal fields, flows, surfaces etc. [1-6]. At phase transitions in liquid crystals, change of space and point-like symmetries of mesophases, structural changes and transformations of the orientational, translational and/or positional order take place. Such transformations of the order parameters are attend with changes of the thermo-morphologic, thermotropic, thermo-optical etc. properties [7-11].

In technical devices based on liquid crystalline materials, these materials are placed between reference surfaces of the sandwich-like cells or displays with various and strongly determined thicknesses. Therefore the topics, which are connected with effect of surfaces and boundary conditions on physical properties of liquid crystalline materials and on the thermotropic peculiarities of phase transitions are important from both fundamental and application points of view [12-16]. Additionally, liquid crystalline devices (displays, indicators, multimatrix elements etc.) use at different thermal regimes, in various temperature intervals and in different climatic conditions.

Therefore information about the thermal properties of liquid crystals is very important.

In this work, we are interested in the effect of boundary conditions on the thermotropic and thermo-morphologic properties of the heterophase regions of phase transitions between nematic mesophase and isotropic liquid in 4-n-alkyl-4'-cyanobiphenyl liquid crystals with different length of the alkyl chain. Namely, we are interested in effect of thickness of liquid crystalline layer, placed between reference surfaces of the sandwich-like samples, on above mentioned properties. Comparative estimations of the temperature and linear widths of the heterophase regions of above mentioned phase transition in the sandwich-cells with various thicknesses have been made. Such investigations were possible only using our original method of the capillary temperature wedge.

2. Experimental

2.1. Materials

In this work, 4-n-alkyl-4'-cyanobiphenyl liquid crystals have been used. 4-n-hexyl-4' cyanobiphenyl (6CB), 4-n-heptyl-4'-cyanobiphenyl (7CB) and 4-n-octyl-4'-cyanobiphenyl (8CB) liquid crystalline materials were objects of our investigations. The structural formula of 4–n–alkyl–4'–cyanobiphenyls is given in Scheme 1. These materials exhibit nematik mesophase and display phase transition between nematic mesophase ans isotropic liquid.

6CB, 7CB and 8CB were purchased from TCI (cat. No. C3154 for 6CB, cat. No. H081 for 7CB and cat. No. C3156 for 8CB). The purity of the liquid crystals studies was examined by means of the chromatography technique and their purity was determined not less than 99.0%.

6CB, 7CB and 8CB liquid crystals are mesogenic compounds, which have uniaxial molecular symmetry and good photo (chemical) stability. These compounds also are thermally stable and stable to moisture. Molecules of 4-n-alkyl-4'-cyanobiphenyl compounds can be considered as rigid rods, which have the cylindrical symmetry about the axis of maximum polarizability and also are the central symmetrical with point-like group as the ∞/mm. Besides, these liquid crystals have large dipole moment and can easily form various texture types. Therefore, 4-n-alkyl-4'-cyanobiphenyls are important materials for scientific investigation, and technical and technological applications.
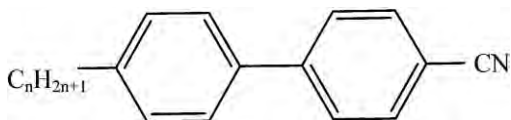
Scheme 1. The structural formula of 4–n–alkyl–4'–cyanobiphenyls. 6CB: n = 6; 7CB: n = 7; 8CB: n = 8

2.2. Method and samples

In this work, the thermo-morphologic and thermotropic properties of the heterophase regions of the phase transition between nematic mesophase and isotropic liquid have been investigated for 6CB, 7CB and 8CB liquid crystals.

Investigation of the thermo-morphologic and thermotropic properties and determination of the temperature widths of the heterophase regions of the nematic mesophase – isotropic liquid (N–I) phase transition have been carried out by the capillary temperature wedge (CTW) device [17,18]. The CTW device is based on the method of temperature wedge [19]. The CTW device was presented in [18-21] and was used for studies of the mesomorphic and thermotropic properties and thermal states of liquid crystalline materials [21-24]. This device allows to obtain simultaneously all of the thermal states of liquid crystalline material in real time scale and also to calculate the temperature and linear widths of the heterophase regions of the phase transitions with accuracy not less as ±10–2 K and ±2.0·10–3 mm, respectively [18-21]. In the CTW device, a homogeneous temperature gradient along the long axis of the sample was performed. The temperature gradient during our measurements has been determined as 1.2 K·mm–1.

For investigations, the sandwich-cells samples as the prolonged plane capillaries were used. Because of the purpose of our investigations was investigations of the thermo morphologic and thermotropic properties of the heterophase regions of the N–I transition vs. thicknesses of liquid crystalline layer, the sandwich-cell samples with various thicknesses were used. These thicknesses as 20 ± 0.1 μm, 60 ± 0.1 μm, 120 ± 0.1 μm and 180 ± 0.1 μm were

chosen. The liquid crystals under investigations were filled into the sandwich-cells by the capillary forces at the isotropic liquid state.

3. Results and discussion

In this work the morphologic properties of 6CB, 7CB and 8CB liquid crystals for various thickness of liquid crystalline layer have been investigated. As an example, in Fig.1 typical textures for 7CB are presented. As seen in this figure, typical textures and their morphologic properties of N mesophase depends on the thickness of liquid crystalline layer. Namely, in sample with thin liquid crystalline layer droplets on the homeotropic background were observed (Fig.1a,b). Availability of the homeotropic alignment is connected with an influence of reference surfaces on liquid crystalline layer and is sufficiently typical behavior of 4-n-alkyl-4'-cyanobiphenyl mesogens, which have tendency of formation of the homeotropic alignment in the sandwich-cells.
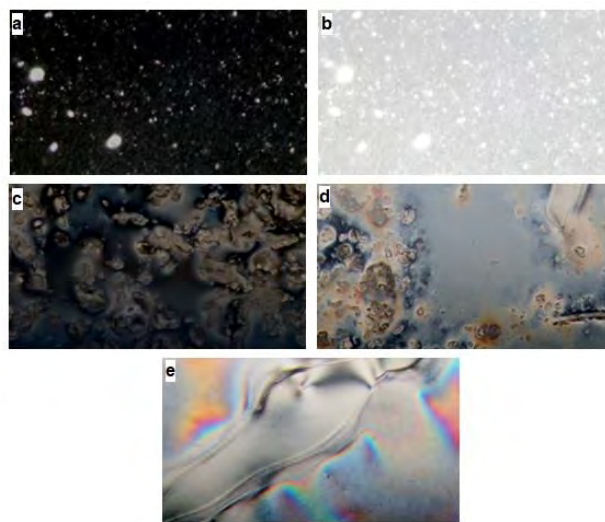

Fig. 1. Typical textures of N mesophase with various thickness of liquid crystalline layer. 7CB liquid crystal. Crossed polarizers. Magnification x100. Temperature 299.0 K.; a – 20 μm, crossed polarizers; b – 20 μm, parallel polarizers; c – 60 μm crossed polarizers; d – 120 μm crossed polarizers; e – 180 μm crossed polarizers

In samples with thickness of the layer as 60 μm because of a decrease an influence of the reference surfaces, regions of the tilted alignment were observed (Fig.1c). With an increase of thickness of liquid crystalline layer, regions with quasi-planar alignment were arisen (Fig.1d). In samples with sufficiently thick liquid crystalline layer, texture, which is presented in Fig.1e, was observed. The colours in presented figure indicate on stratification of N mesophase structure and are connected with difference path in different regions of this texture. These results indicate on sufficient effect of thickness of liquid crystalline layer on morphologic properties of liquid

crystalline materials. Therefore, is clear that for identification and classification of liquid crystalline mesophases by type of liquid crystalline textures is necessary to take into consideration the thickness of liquid crystalline layer.

In this work the thermo-morphologic and thermotropic properties of the heterophase regions of the phase transitions between N mesophase and isotropic liquid in 6CB, 7CB and 8CB liquid crystals have been also investigated for various thicknesses of liquid crystalline layer. As is known, phase transitions in liquid crystals are accompanied by the heterophase regions. These regions have important meaning from both fundamental and application points of view. In the heterophase regions the low temperature phase and high temperature phase simultaneously coexist. These regions are characterized by strongly definite temperature interval as $\Delta T = T^{**} - T^*$. Availability of the heterophase regions and the T^{**} and T^* temperatures was predicted in frames of the Landau-de Gennes theoretical model [25-27]. The T^{**} and T^* are the temperature limits of the heterophase region. At the T^*, low temperature phase (more regulated liquid, i.e. crystalline mesophase) is stable, but high temperature phase (less regulated mesophase, i.e. isotropic liquid) is metastable. The T^* and T^{**} temperatures can be calculated as [20,28-30]

$$T^* = T_{NI} - \frac{2B^2}{9aC} \tag{1}$$

$$T^{**} = T_{NI} + \frac{B^2}{36aC} \tag{2}$$

Here TNI is temperature of phase transition between N mesophase and isotropic liquid; the *a*, *B* and *C* are coefficient of the free energy free distribution, whish are depend on temperature and pressure. The free energy in terms of the Landau-de Gennes model for above mentioned phase transition can be written in the form of [25-27,31]

$$F = F_0 + \frac{1}{2}AQ^2 - \frac{1}{3}BQ^3 + \frac{1}{4}CQ^4 \tag{3}$$

Here the F_0 value is the free energy of isotropic liquid state. Note that the *a* and *A* parameters are connected as $A=a(T-T^*)$. At $T<T_{NI}$ temperature, one minimum by $Q=0$ takes place for the $F(Q)$ dependence; this case corresponds to N mesophase. At $T=T_{NI}$ temperature, two minimums by $Q=0$ and $Q\neq0$ take place for the $F(Q)$ dependence; in this case $Q\neq0$ corresponds to N mesophase and $Q=0$ corresponds to isotropic liquid state. At $T>T_{NI}$ temperature, one minimum by $Q=0$ takes place for the $F(Q)$ dependence; this case corresponds to isotropic liquid state. Besides, in accordance with the Landau-de Gennes model at the $T=T^*$ temperature

$$Q = \frac{B}{2C} \tag{4}$$

and at the $T = T^{**}$ temperature

$$Q = \frac{B}{4C} \tag{5}$$

take place.

Our investigations showed that change of thickness of liquid crystalline layer has effect on the thermo-morphologic and thermotropic properties of the heterophase regions of the I–N phase transitions in 6CB, 7CB and 8CB. As an example, in Fig.2 microphotographs of the heterophase regions of the above mention phase transitions for 7CB liquid crystal are presented. As seen in this figure, the thermo-morphologic properties of the heterophase regions are depend on thickness of liquid crystalline layer. Namely, textures of N mesophase near the N–I phase transition are sufficiently different in samples with different thickness of liquid crystalline layer. Such morphology of N mesophase in the heterophase region is connected with character of the forming of N mesophase phase during cooling process from isotropic liquid state to N mesophase and with character of transformation of isotropic state with symmetry as K_∞ to N mesophase ordering with symmetry as $D_{\infty h}$.
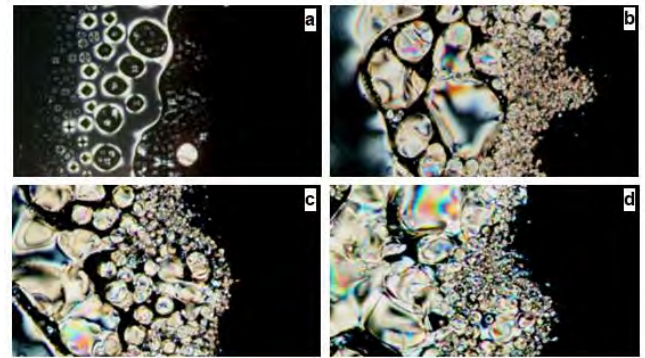

Fig. 2. The heterophase regions of the I–N phase transitions for samples with various thickness of liquid crystalline layer. 7CB liquid crystal Crossed polarizers. Magnification x100. a – 20 μm; b – 60 μm; c – 120 μm; d – 180 μm. By the pointer, temperature gradient from T₁ temperature to T₂ temperature (T₂> T₁) is indicated

We would like to emphasize, that as is seen in Fig.2d, in region of the I–N phase transition for thick samples as 180 μm the petal-like formations are observed. Additionally, in Fig.3 such formations for samples with the same thickness are presented. Such type of formations usually was observed for the layered liquid crystalline mesophase [32-34]. Appearance of the petal-like formations in N mesophase at the I–N phase transition obviously is connected with appearance some liquid crystalline layers in thick samples. This is confirmed by an occurrence of colored regions (Fig.3), which are connected with difference path in regions with different colors. Besides, as can see in Fig.3, defects as the inversion walls and singular points with the disclination of the strength as |S| = 1 take place in the heterophase region. Such defects usually appear in volumetric samples.
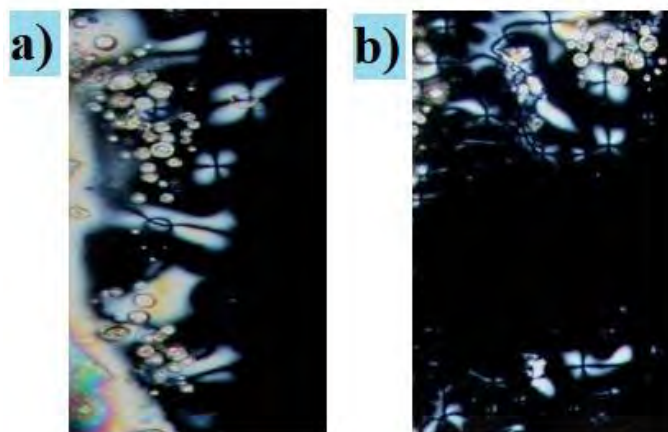
Fig. 3. The petal-like formations and colored regions in N mesophase at I–N phase transitions. 7CB liquid crystal Crossed polarizers. Magnification
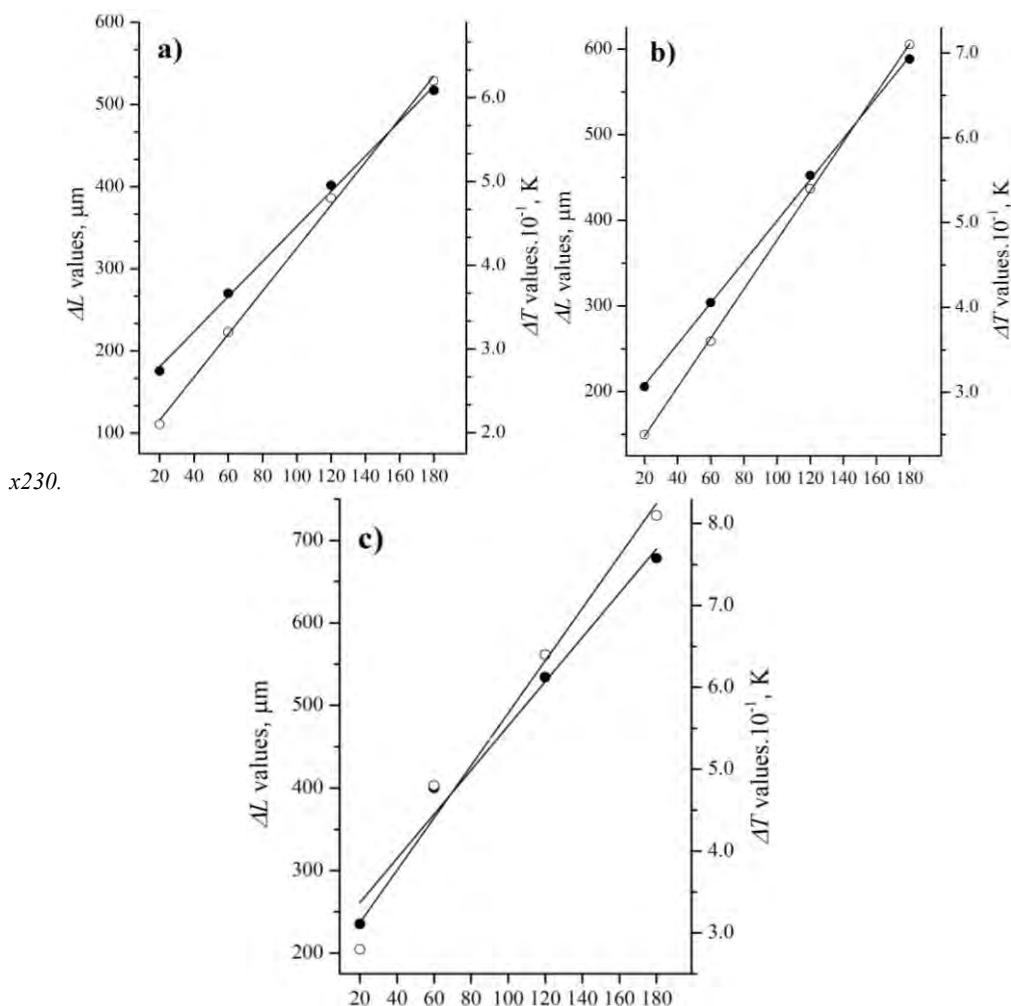
x230.

Fig. 4. Temperature and linear widths of the heterophase regions for 6CB, 7CB and 8CB liquid crystals vs. thicknesses of liquid crystalline layer. A Plate – 6CB; B Plate – 7CB; C Plate – 8CB. ○ –   values; • –   values.

In this work using the CTW method, temperature and linear widths of the heterophase regions of I–N phase transitions for 6CB, 7CB and 8CB liquid crystals were determined. Results of such determinations are tabulated in Table 1. As seen in this table, change of thickness of liquid crystalline layer has effect on the thermotropic properties of the heterophase regions of the I–N phase transitions. Namely, by an increase in thickness of liquid crystalline layer the widening of the temperature and linear widths of the heterophase regions for liquid crystals under

investigations has been found. Besides, the linear and temperature widths of the heterophase regions for 8CB are larger than that for 6CB. Obviously, such differences in the heterophase regions for 6CB and 8CB are connected with differences in the alkyl chain of 6CB and 8CB. As also seen in Table 1, the differences between the temperature and linear widths of the heterophase regions in the thin and thick samples are as 0.41 K and 341.7 μm for 6CB, 0.459 K and 382.6 μm for 7CB and 0.532 K and 443.0 μm for 8CB. In Fig.4, dependences of the temperature and linear widths of the heterophase regions for liquid crystals under investigations are presented. As seen in this figure, by an increase of thickness of liquid crystalline layer, monotonous increase of the *ΔT* and *ΔL* values occur. Such behavior of the *ΔT* and *ΔL* values vs. thicknesses of liquid crystalline layer indicates on linear dependence of the thermotropic properties of liquid crystals under investigations on these thicknesses.

Table 1. Features of thermotropic properties of the heterophase regions for 6CB, 7CB and 8CB liquid crystals

Liquid Crystal	Thickness of liquid crystalline layer, μm	Linear widths of the heterophase regions (ΔL), μm	Temperature widths of the heterophase regions (ΔT), K
		I→N transition	I→N transition
6CB	20	175.5	0.21
	60	270.0	0.32
	120	401.3	0.48
	180	517.2	0.62
7CB	20	205.5	0.25
	60	303.7	0.36
	120	452.3	0.54
	180	588.1	0.71
8CB	20	235.2	0.28
	60	400.0	0.48
	120	534.3	0.64
	180	678.2	0.81

Thus, the results, which are obtained in our investigations, show that the change of thickness of liquid crystalline layer has a sufficient effect on the thermo-morphologic and thermotropic properties of the heterophase regions of phase transitions between N mesophase and isotropic liquid. This effect is obviously connected with the character of interaction between liquid crystalline molecules and reference surfaces of the sandwich-cell. I.e. this effect is connected with the change of the liquid crystalline molecules – surfaces interaction energy vs. change of thickness of liquid crystalline layer. As is known, two cases of such interactions as the strong coupling and the weak coupling take place for liquid crystalline molecules – surfaces interaction [2,26,27,35]. These anchoring types are characterized by the interaction energy *W* and the extrapolation length *b*. Connection between *W* and *b* is determined by [2,15,26]

$$W = \frac{L}{b} \qquad (6)$$

Here *L* is length of molecule of N mesophase. In the case of the weak coupling, the energy of interaction between molecules of N mesophase is bigger than the

energy of interaction between molecules of N mesophase and the reference surfaces. In this case, the *W « 1* and *b »* L connections take place. By such coupling the thermo-morphologic and thermotropic properties of N mesophase are determined by the interaction between molecules of N mesophase. In the case of the strong coupling, the energy of interaction between molecules of N mesophase is smaller than the energy of interaction between molecules of N mesophase and the reference surfaces. In this case, the W → ∞ 1 and b « L connections take place. By such coupling, near the lower and upper reference surfaces of sandwich-cell, the boundary layers are arisen [25,26,36-38]. Therefore, in this case the thermo-morphologic and thermotropic properties of N mesophase are determined by these boundary layers in the sandwich-cell. In Fig.5, schematic representation of the extrapolation length is given. As seen this figure, by the smaller coupling the bigger extrapolation length takes place. And for samples under investigations with different thicknesses of liquid crystalline layer, by an increase of the thickness a decrease of the W values and an increase of the b values take place.
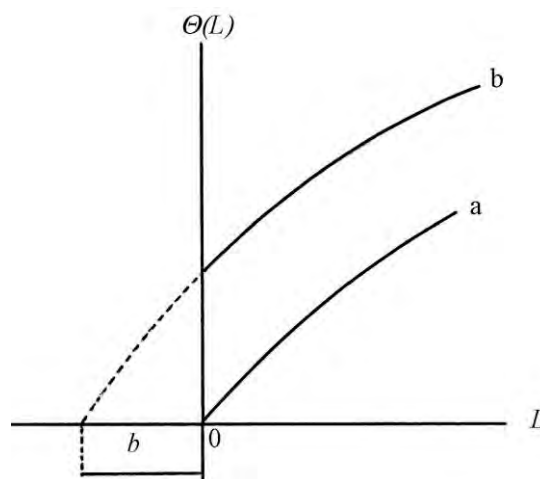

Fig. 5. Schematic representation of the extrapolation length. a – the strong coupling,b=0; b – the weak coupling,b≠0. Θ(L)is rotational angle, which is depend on thickness of liquid crystalline layer

4. Summary

Our investigations showed that thickness of liquid crystalline layer has sufficient effect on the thermo-morphologic and thermotropic properties of the I–N phase transition and on the temperature and linear widths of the heterophase regions of this phase transition.

The results, obtained in this work, can be shortly summarized as follows:

• Change of thicknesses of liquid crystalline layer, placed between reference surfaces of the sandwich-cell, leads in 6CB, 7CB and 8CB liquid crystals to the transformations of type of liquid crystalline texture and to a change of the morphologic properties of the heterophase region of the I–N phase transition.

- Change of thicknesses of liquid crystalline layer, placed between reference surfaces of the sandwich-cell, leads in 6CB, 7CB and 8CB liquid crystals to a change of temperature and linear widths of the heterophase regions of the I–N phase transition. Namely, an increase in thicknesses of liquid crystalline layer leads to the widening of the linear and temperature widths of the heterophase regions.

- Dependences of the temperature and linear widths of the heterophase regions in 6CB, 7CB and 8CB liquid crystals are connected with differences in character of the interaction between liquid crystalline molecules and reference surfaces of the sandwich-cell with different thicknesses and are also connected with differences of the extrapolation length for thick and thin liquid crystalline layer.

- Values of the temperature and linear widths of the heterophase regions are connected with length of alkyl chain of 4-n-alkyl-4'-cyanobiphenyl mesogens. Namely, liquid crystalline material with longer alkyl chain (i.e. 8CB) exhibits wide heterophase region than that for liquid crystalline material with shorter alkyl chain (i.e. 6CB).

- Effect of thickness of liquid crystalline layer on the temperature and linear widths of the heterophase regions of the I–N phase transition is necessary to take into consideration by studies of physical properties of liquid crystalline materials and by elaboration of liquid crystalline displays and multimatrix elements, which will be used in liquid crystalline thermography.

Acknowledgements

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[*]Corresponding author: narifn.2018@gmail.com