CHANGE OF MESOGENIC PROPERTIES OF LIQUID CRYSTAL 5CB AT THE PRESENCE OF SILVER NANORODS

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Influence of silver nanorods on mesogenic properties of nematic liquid crystal 4- cyano-40-pentylbiphenyl (5CB) is investigated by the methods of differential scanning calorimeter, polarization microscopy, and dielectric spectroscopy. It is shown that the temperature of the nematic-isotropic transition increases. In this case, there is a decrease in enthalpy and entropy of the phase transition at presence of silver nanorods.

Keywords: nematic liquid crystal; silver nanorods; polarization microscopy; differential scanning calorimetry; electric conductivity; dielectric permittivity.
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INTRODUCTION

One of the rapidly developing fields of physics is plasmonics. Plasmon resonance is very sensitive to the environment of corresponding nanostructures. Therefore, the possibility of changing the optical and dielectric properties of the medium is an effective way to control the surface plasmon resonance. Liquid crystals (LC) are suitable candidates for the role of such media.

Dispersion of small amount (0.02 wt.% and 0.05 wt.%) of silver nanoparticles (NP) in nematic LC increases cleaning temperature and the conductivity anisotropy while threshold voltage decreases [1]. It is shown in the work [2] that the existence of dipole–dipole correlation could be the main reason of decreasing of dielectric anisotropy at low concentration (0.25 wt.%) of silver NPs in LC. Methods of Raman spectroscopy and dielectric measurements show that the inclusion of silver NP (0.25 wt.% and 0.50 wt.%) in LC leads to the modification in molecular polarizability of LC and a decrease in magnitude of dielectric anisotropy [3]. Authors of the work [4] observed that the inclusion of small concentration (1 wt.%) of gold NPs into nematic LC decreases switch-on voltage and the relaxation frequency due to internal local electric field generated because of the relative permittivity differences of gold NPs and LC material. Thermodynamical, dielectric, optical and electro-optical characterisation of pure 8CB and its composites with gold and silver nanoparticles have been studied in the work [5]. It was shown that clearing temperature, threshold voltage for Freederick transition, switching voltage, splay elastic constant, and the optical band gap decrease while ionic conductivity, relaxation frequency and activation energy increase. Dielectric anisotropy is almost unchanged for both the nanocomposites. It is shown in the work [6] that the dispersion of Ag NPs (0.5 wt./wt.%, 1 wt./wt.% and 2 wt./wt.% (into nematic LC 4′-(Octyloxy)-4-biphenylcarbonitrile leads to the change in physical parameters such as dielectric permittivity, photoluminescence, threshold voltage, response time and splay elastic constant. The AC conductivity and threshold voltage of Ag NPs-dispersed composite system have increased significantly.

The liquid crystal 5CB doped with alkylthiol-capped gold NPs (0.1 -5 wt.%) has been investigated in the work [7]. It is shown that the nematic–isotropic transition of the composite decreases nearly linearly with increasing concentration of NP. At this case, the electrical conductivity of the system increases by more than two orders of magnitude.

The negligible change is observed in the value of birefringence for the lower doping concentration ($\leq$ 0.5 wt%) of silver nanorods in nematic LC by the authors of the work [8]. The parallel and perpendicular components of dielectric permittivity increase with the addition nanorods. The conductivity increases at the doping concentration of 0.2 wt% however decreases with further increase in the doping concentration because of the trapping of ionic impurities by of silver nanorods.

The aim of the work is to study mesogenic properties of liquid crystal 5CB at presence of silver nanorods.

EXPERIMENTAL

We used nematic liquid crystal 4-cyano-40-pentylbiphenyl (5CB) from the firm Merck with positive dielectric anisotropy as a matrix. The temperature range of the nematic phase of this LC is usually located between 21.3^0C and 35.2^0C.

The silver nanorods (US, Research Nanomaterials, In.) had diameters of 2-5 nm and lengths of 10-20 nm. They were dispersed into ethanol then the mixture was added into the liquid crystal. The obtained mixture was shaken in a vortex mixer for 6 hour at temperature 40^0C until the ethanol is completely evaporated, The resulting mixture with concentration of 0.2 wt.% was induced by sonication with dispergator Ultrasonic Cleaner NATO CD-4800 (China) for 4 hours.

The differential scanning calorimeter DSC 204 F1 (firm Netzsch, Germany) with the CC200 F1

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cooling system regulating the flow of liquid nitrogen was used to determine thermo-physical parameters. Argon was served to purge and to protect the cell at the pressure of 50 kPa. The DSC204F1 and Proteus Analysis software program was used to process the results. The rate of temperature change was 5 K/min in the temperature range between 0^0C and 45^0C.

The critical temperature T, at which the composite changes from one state to another, was determined by the local maximum of the heat flow while the change in enthalpy ΔH was defined by the expression:

$$\Delta H = k \cdot \Delta A, \quad (1)$$

where k is characteristic for this device, A is the area under the corresponding peak. The entropy change ΔS during transition was defined as:

$$\Delta S = \frac{\Delta H}{T}. \quad (2)$$

The images of colloid textures were observed under the Carl Zeiss polarisation microscope (model 720, Germany).

Dielectric and conductivity measurements were carried out by the Precision LCR Meter 1920 (IET Labs. Inc., USA) at the frequency of 1 kHz and at temperature range between 22^0C - 45^0C. The cell had a sandwich structure and consisted of two plane-parallel glass plates whose inner surfaces were coated with thin transparent and conductive indium-tin-oxide (ITO) layer. Planar orientation of molecules was attained by coating the inner substrate surfaces with rubbed polyimide layers. For obtaining of homeotropic orientation of LC molecules, we used the surfactant (polysiloxane). The cell thickness was fixed with calibrated 20 μm polymer spacers for measurements. Both the colloid and the pure LC were injected into the empty cell by capillary action at the isotropic state. To increase the dispersion, the cells with the colloid were placed at electric field of 40V to achieve turbulence and were kept for 2 days. In this case, no aggregation of particles was observed. The filled cell was kept in the special heater with temperature regulator GL-100 (China). The copper-constantan thermocouple was used for temperature control. An accuracy of temperature determination was 0.1^0C. In such a case, applied voltage was 0.5V for both LC molecular orientations. Electric capacity C and dissipation factor (the loss tangent) *D* were recorded by means of this device at frequency *f* of 1 kHz. The magnitudes of dielectric permittivity *ε* were defined as:

$$\varepsilon = \frac{C}{C_0}, \quad (3)$$

where C_0 is the electric capacity of the empty cell. The real ε' and image ε'' parts of dielectric permittivity and electric conductance σ were calculated by the expressions:

$$\varepsilon' = \frac{\varepsilon}{\sqrt{1+D^2}}, \quad (4)$$

$$\varepsilon'' = \frac{\varepsilon D}{\sqrt{1+D^2}}, \quad (5)$$

$$\sigma = 2\pi f \varepsilon_o \varepsilon'', \quad (6)$$

RESULTS AND DISCUSSION

Figure 1 shows the DSC curves of both the pure LC and the colloid at heating and cooling regimes.

First, it can be seen from Fig. 1 that the pronounced DSC peak of the pure LC is observed at the heating regime, the maximum of which conforms with temperature of the transition from crystalline phase to LC one while the corresponding peak is weak at the cooling regime.

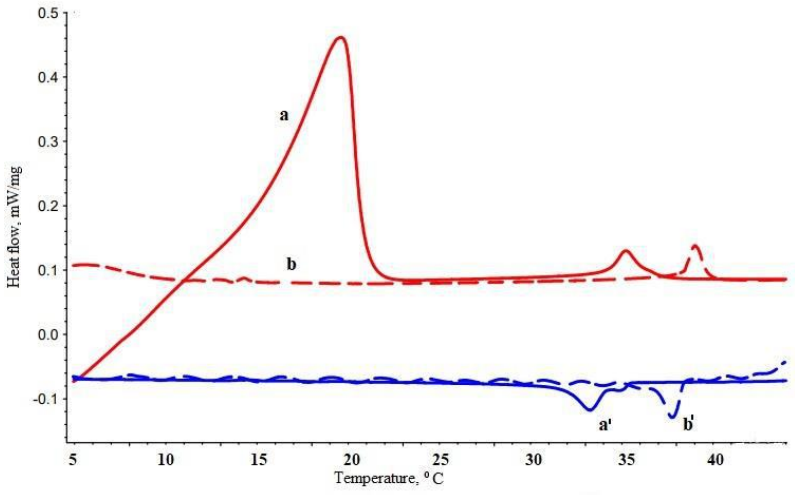

Fig.1. Dependence of heat flow on temperature: (a) the pure LC at heating regime; (a′) the pure LC at cooling regime; (b) the colloid at heating regime; (b′) the colloid at cooling regime.

The DSC peak of the transition from the crystalline to the liquid-crystalline state of the colloid is not observed at the investigated temperature range. It indicates that the presence of nanorods prevents the corresponding transition. The critical point of the phase transition from the LC state to the isotropic one shifts to higher temperatures at both the heating regime and the cooling regime with the additive of nanorods. Moreover, the transition temperature at cooling regime is lower relative to the heating one. It is obvious that there is overcooling of the material.

Figure 2 shows images under the polarizing microscope of both the pure LC and the colloid near the transition from the LC state to the isotropic one.

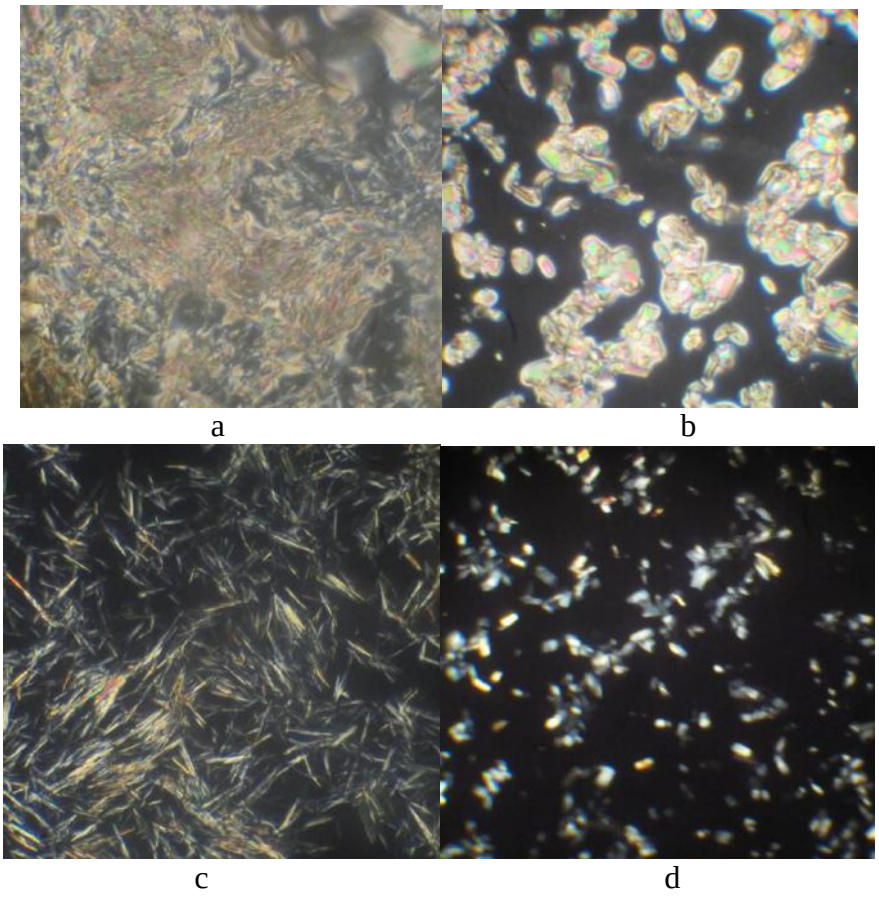

Fig. 2. Texture images under the polarizing microscope (1500 x magnification): (a) the pure LC at 34.1°C, (b) the pure LC at 34.9°C, (c) the colloid at 38.3°C, (d) the colloid at temperature 39.2°C.

As can be seen, light anisotropic areas of the pure LC texture gradually give way to dark isotropic areas in the vicinity of the phase transition (Fig. 2a and Fig. 2b). Filamentous light areas are observed for the colloid at temperature of 38.3°C (Fig.2c), which is much higher than the clearing temperature of the pure LC. It indicates that anisotropic areas near the nanorods are retained at this temperature. According to [7], LC molecules rigidly adhere to the surface of nanorods. This anchoring is maintained up to temperature of 39.0°C. Thus, the clearing point shifts to higher temperatures. It is also indicated by the temperature dependences of permittivity and electrical conductivity of the colloid (Fig. 3 and Fig. 4). It can be seen from Fig. 3 that there are different values of the longitudinal and transverse components of permittivity of the pure LC up to 35.2°C. It indicates that the substance exists in the liquid-crystalline state at indicated temperatures. We also note that the longitudinal component of the permittivity decreases while the transverse component increases in comparison with the corresponding components of the pure LC. It indicates on a decrease in the dielectric anisotropy and the order parameter which are compatible with the results of differential scanning calorimetry and polarization microscopy. After this temperature, the transverse and longitudinal components of the permittivity become equal. That is, the molecules exist in a chaotic isotropic state. An analogous situation is observed for the colloid but at temperature of 39.0°C.

Similar analysis can be carried out for temperature dependences of conductivity. Here, It can also be seen that the equalization of the transverse and longitudinal conductivity components for the pure LC occurs at temperature of 35.2°C while it takes place at temperature of 39.0°C in the colloid. That is, the results of the measurements of the temperature dependences of the conductivity of the pure LC and the colloid agree with the previous experiments. We also note that the additive of nanorods increases the conductivity of LC. Obviously, it ensues owing to the increase in the conductivity of the ionic and electronic components because of the presence of metal particles.

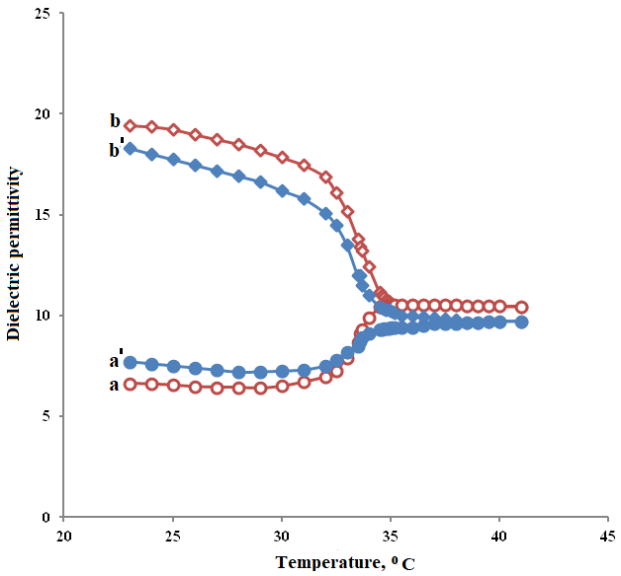

Fig 3. Temperature dependence of components of dielectric permittivity at the frequency of 2 kHz: (a) the longitudinal component of the pure LC, (a') the longitudinal component of the colloid, (b) the transverse component of the pure LC, (b') the transverse component of the colloid.

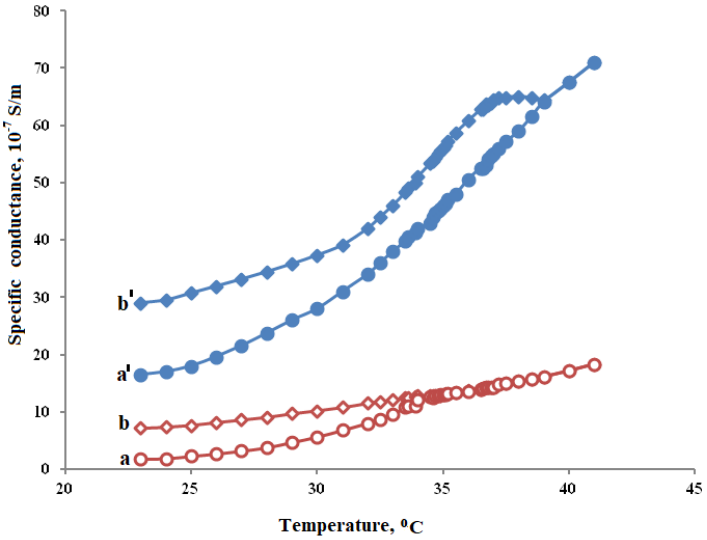

Fig. 4. Temperature dependences of specific conductance at the frequency 2 kHz: (a) the longitudinal component of the pure LC, (a') the longitudinal component of the colloid, (b) the transverse component of the pure LC, (b') the transverse component of the colloid.

Table 1 shows the numerical values of the critical temperature of transitions from the crystalline to the liquid crystalline state T_1 and the liquid crystalline to the isotropic state T_2 as well as the change in enthalpy (ΔH_1 and ΔH_2) and entropy (ΔS_1 and ΔS_2) at heating and cooling regimes calculated from Fig.1.

Table 1.

Values of the critical temperature of transitions from the crystalline to the liquid crystalline state T_1 and the liquid crystalline to the isotropic state T_2 as well as the change in enthalpy (ΔH_1 and ΔH_2) and entropy (ΔS_1 and ΔS_2) at heating and cooling regimes.

		T_1, °C	ΔH_1, J/g	ΔS_1, mJ/g ·K	T_2, °C	ΔH_2, J/g	ΔS_1, mJ/g ·K
Pure LC	heating	19.6	76.880	262.75	35.2	2.644	8.58
	cooling	14.3	0.108	0.383	33.3	-2.642	-8.62
Colloid	heating	0	0	0	39.0	2.315	7.42
	cooling	0	0	0	37.7	-1.844	-5.93

The change of thermodynamic functions is the most interesting for transition from liquid crystalline to isotropic state. As can see the change in enthalpy when adding nanorods decreases in both regimes at additive of nanorods. Moreover, it is less in the cooling regime than in the heating one.

It is known that the change of enthalpy is the energy that is absorbed or emitted as heat from a substance when it changes from one state to another and it occurs without changing of the temperature. It serves to disorganize the intermolecular bonds that hold molecules together. During curing, the reverse process (endothermic) occurs in which heat is removed from the substance. In this case, intermolecular bonds are restored, and the temperature does not change. A decrease of the change in enthalpy at both in the heating regime and the cooling one, indicates that the presence of nanorods reduces the interaction between the molecules of the LC.

The entropy of phase transition is a measure of the disorder of the substance accompanying this transition. It is sensitive to change of the arrangement of molecules and their configuration. As can be seen from Table 1, the entropy of the transition decreases with the additive of nanorods. It indicates on a decrease in the difference of the disorder degree between the liquid crystalline state and the isotropic one due to the presence of nanorods. As a result, the disorder of the liquid crystalline state of the colloid is greater than the pure LC. It is consistent with the results of dielectric measurements.

CONCLUSION

It was shown that presence of silver nanorods increase the cleaning temperature and decreases of enthalpy and entropy of transition from nematic phase to isotropic on nematic liquid crystal 5CB.

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