INFLUENCE OF SINGLE-WALLED CARBON NANOTUBES ON DIELECTRIC AND CONDUCTIVITY PROPERTIES OF SMECTIC *A* LIQUID CRYSTAL WITH NEGATIVE DIELECTRIC ANISOTROPY

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It was experimentally obtained that the presence of single-walled carbon nanotubes with concentration of 0.5% in the smectic liquid crystal with negative dielectric anisotropy reduces the transition temperature from the smectic to isotropic state. Both the longitudinal and transverse components of dielectric permittivity and the dielectric anisotropy are shown to increase in the presence of nanotubes. At the same time, the resulting percolation effect contributes to the increase in conductivity.

1. INTRODUCTION

Single-walled carbon nanotubes (SWCNTs) have a diameter comparable to cross-section of elongated liquid crystal (LC) molecules. Rod-like particles of SWCNTs in nematic LC cause the effective orientational coupling with LC molecules [1]. The charges transfer from LC molecules to the particles and they are distributed asymmetrically on the SWCNTs inducing a permanent dipole moment on them [2, 3]. As a result, SWCNTs are oriented parallel to the LC director enhancing the orientation order and consequently, the display parameters of composite systems improved [3-5]. Moreover, liquid crystals provide a medium for controlling the alignment of carbon nanotubes [6].

It was shown in [7-9] that the inclusion of SWCNTs in the nematic matrix with positive dielectric anisotropy increases the nematic-isotropic transition temperature. In this case, the dielectric anisotropy increases and the threshold voltage decreases at tiny amount (0.01-0.02 wt. %) of SWCNTs [7-9]. In the works [10-11], SWCNTs were dispersed in nematic liquid crystal 4-pentyl-4′-cyanobiphenyl at the concentration of 0.02 and 0.05 wt%. Differential scanning calorimetry and temperature-dependent dielectric studies suggest decrease in clearing temperature of the composite materials as compared to the pure material. Ionic conductivity increases by two orders of magnitude due to the dispersion of such a low concentration (0.05 wt%) of SWCNTs. Dielectric studies also show that the presence of the SWCNTs decreases the effective longitudinal as well as transverse components of the dielectric permittivity. From frequency-dependent dielectric studies, important dielectric parameters such as relaxation frequency, dielectric strength and distribution parameters have been determined. Electro-optical experiments show that the threshold voltage decreases and the steepness of the transmission voltage curve improves due to the dispersion of SWCNTs. Presence of SWCNTs increases the relaxation frequency corresponding to flip-flop motion of molecules around

their short axes. A significant enhancement in the dielectric anisotropy and conductivity of SWCNTs doped p-ethoxybenzylidene *p*-butylaniline nematic LC at concentration of 0.01 and 0.02 wt.% was observed in the work [12].

The photoresponsive electro-optical composites based on the cholesteric liquid crystal with optically controlled chirality and a minute amount of SWCNTs are studied in [13]. It is found that this composite demonstrates dual-mode operation with optical switching between reversible and memory mode. Authors of the work [14] studied the conductivity and dielectric anisotropy change in cholesteric LC system doped with SWCNTs. The results lead to the conclusion that the enhancement of the electrical conductivity and the change of the dielectric anisotropy in the SWCNT doped cell is mainly caused by the aligning effect of cholesteric liquid crystal system. It was shown in [15] that the inclusion of SCNTs significantly affect on the dielectric parameters in the chiral smectic *C* phase with an inversion of the effect near the transition to, and in, the chiral smectic *A* phase. It is demonstrated in [16] that even a small amount of chiral SWCNTs affects greatly on the performance of ferroelectric liquid crystal cells. Particularly, the spontaneous polarization, the Goldstone mode dielectric strength and the rise time are decreased in doped cells. Under high electric field, highly concentrated SWCNT doped ferroelectric LC shows enormously large values of dielectric loss [17]. This is due to the high conductivity of SWCNT at higher electric field. Influence of SWCNTs on the re-entrant phenomenon in LCs has been studied in [18]. Here a small concentration (0.5 wt. %) of SWCNTs doped to a nematic material not only induces the layered smectic A mesophase but also leads to the nematic-smectic-nematic re-entrant sequence.

It is known that continuous network of SWCNTs is formed in the LC colloid at a certain concentration. The structural percolation transition takes place for LC doped with SWCNTs at concentrations between 0.02 and 0.2 wt % [19].

The aim of this work is to study the effect of

SWCNTs at concentration of 0.5wt.% on the dielectric and conductivity properties of smectic A liquid crystal 4-hexyloxyphenyl ether of 4'-hexyloxy-3'-nitrobenzoic acid.

EXPERIMENTAL

We used smectic *A* liquid crystal 4-hexyloxyphenyl ether of 4'-hexyloxy-3'-nitrobenzoic acid with negative dielectric anisotropy as a matrix.

The temperature range of smectic phase is located between 30°C and 71°C. A presence of nitrophenyl dipole group $-C-NO_2$ of this LC is the reason of the large negative dielectric anisotropy.

The single-walled carbon nanotubes (US, Research Nanomaterials, In.) were added into the liquid crystal with concentration of 0.5 wt.%. Then obtained mixture was shaken in a vortex mixer for 1 hour at temperature 80°C, followed by sonication with dispergator Ultrasonic Cleaner NATO CD-4800 (China) for 4 hours.

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 40 V to achieve turbulence and were kept for 2 days. In this case, no aggregation of particles was observed. The stuffed 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°C.

Dielectric and conductivity measurements were carried out by the Precision LCR Meter 1920 (IET Labs. Inc., USA) in the frequency range of 20 Hz – 1MHz. In this case, applied voltage was 0.5 V for both LC molecular orientations.

2. RESULTS AND DISCUSION

Observation of the change in texture under a polarizing microscope shows that the appearance of dark areas in the liquid crystal and the colloid is observed at temperatures of 70.9°C to 68.3°C, respectively. It indicates that the clearing points for the pure liquid crystal and the colloid occur at the indicated temperatures.

Fig. 1 shows the dependences of real ε' and imaginary ε'' parts of dielectric permittivity of the pure liquid crystal and the colloid at planar configuration at temperature 32°C. As seen, ε' of the pure LC decreases from the value of 14.02 at 40 Hz to 13.20 at 2 kHz, then it decreases sharply after 30 kHz. Values of ε' for the colloid are greater than for the pure LC at all frequencies. It varies from 15.52 at 40 Hz to 15.33 at 2kHz, then its value also decreases sharply after 30 kHz. The presence of nanotubes increases the values of ε''. In this case, the dielectric absorption maximum shifts to the low-frequency region from 200 kHz to 130 kHz.

It is known that the relaxation time of LC molecules which is characterized by their overturn from one to the opposite direction, is determined by the ratio

$$\tau = \frac{1}{2\pi f} \qquad (1)$$

where f is the frequency of the applied electric field. The additive of nanotubes increases the relaxation time from $8.0 \cdot 10^{-7}$s to $1.22 \cdot 10^{-6}$s at 32°C. The increase in the relaxation time indicates that the single-walled carbon nanotubes in the liquid crystal prevent the flip-flop motion of the molecules. It promotes to an increase in rotational viscosity for the colloid.

The frequency dependences of the real and imaginary parts of dielectric permittivity for the pure LC and the colloid at homeotropic configuration and temperature 32°C are presented in fig. 2. As can be seen, ε' of the pure LC is equal to 4.25 at 40 Hz, then there is a dispersion near 500 Hz and its value remains almost unchanged and equal to 3.91 up to 100 kHz then decreases sharply. The additive of nanotubes increases value of ε' to 4.90 at 40 Hz and 4.78 at 2 kHz. Here the dispersion is also observed near the frequency of 1 kHz. The dielectric absorption maximum of the pure LC and the colloid is observed around 500 Hz. Obviously, this dispersion is connected with dipole fragment $-C-NO_2$, which is not strictly perpendicular to the long axis of the molecules, but has a component parallel to its long axis. It should be noted that the dielectric anisotropy of the pure LC is -9.75 at the frequency of 40 Hz while this value is -10.23 for the colloid. Note also that the dielectric anisotropy of liquid crystal is -9.29 at 2 kHz while it is -10.55 for the colloid. That is, the dielectric anisotropy increases with the additive of particles.

It is known that the gap between the layers of smectic LC have a width greater than the transverse dimension of nanotubes. Therefore, a part of nanotubes is located between layers. An another part of nanotubes is located along the predominant direction of LC molecules. Exactly this part of nanotubes interacts with LC molecules. This interaction is dipole-dipole, as asymmetric molecules of the liquid crystal induce asymmetric arrangement of charges on nanotubes turning them into dipoles. In the same time, the ordered arrangement of the LC molecules is improved. In this case, the dipole of the LC molecule directed at an angle of 60° to the long axis of the molecule, plays a special role. In this connection, it is not possible to judge the change in the order parameter.
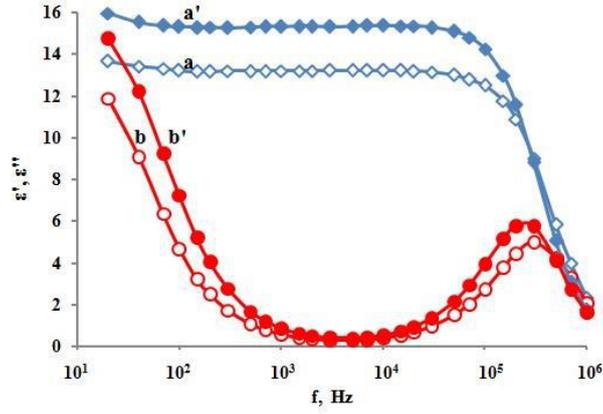
Fig.1. Frequency dependences of real ε' and imaginary ε'' components of dielectric permittivity at planar configuration (temperature 32°C): (a) ε' of the pure liquid crystal, (a') ε' of colloid, (b) ε″ of the pure liquid crystal, (b') ε″ of the colloid.
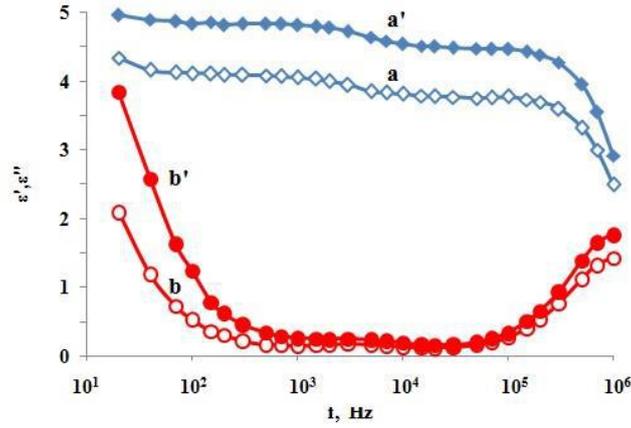
Fig.2. Frequency dependences of real ε' and imaginary ε'' components of dielectric permittivity at homeotropic configuration and 0.5% concentration (temperature 32°C): (a) ε' of the pure liquid crystal, (a') ε' of the colloid, (b) ε′ of the pure liquid crystal, (b') ε′ of the colloid.

In rough approximation, the Maier-Meier theory can be used to analyze the results of dielectric measurements of the smectic LC, although this theory was developed for nematic liquid crystals. According to this theory, the dielectric permittivity components are defined as [20]:

$$\varepsilon'_{\text{II}} = 1 + \frac{NHF}{\varepsilon_0}\left\{\gamma_{av} + \frac{2}{3}S\Delta\gamma + F\frac{p_e^2}{3k_BT}\left[1 - \left(1 - 3\cos^2\beta\right)S\right]\right\} \tag{2}$$

$$\varepsilon'_{\perp} = 1 + \frac{NHF}{\varepsilon_0}\left\{\gamma_{av} - \frac{1}{3}S\Delta\gamma + F\frac{p_e^2}{3k_BT}\left[1 + \frac{1}{2}\left(1 - 3\cos^2\beta\right)S\right]\right\} \tag{3}$$

and the dielectric anisotropy is given by:

$$\Delta\varepsilon' = \frac{NHF}{\varepsilon_0}\left[\Delta\gamma - F\frac{p_e^2}{2k_BT}\left(1 - 3\cos^2\beta\right)\right]S \tag{4}$$

where F is reaction field factor, H is the cavity form factor, $\gamma_{av} = (\gamma_{II} + 2\gamma_{\perp})/3$ is the average value of polarizability of LC molecules, $\Delta\gamma = \gamma_{II} - \gamma_{\perp}$ is the anisotropy of polarizability, N is the number of LC molecules per unit volume, S is the order parameter, β is the angle between the point molecular dipole p_e and the axis of maximum molecular polarizability, ε_0 is

dielectric permittivity of vacuum, k_B is Boltzmann constant, T is Kelvin temperature.

Since the dipole moment of this LC is directed at an angle of 60° to its long axis, respectively, to the direction of maximum polarizability, that is, angle β=60°, $cos\beta$=1/2 and 1-3$cos2\beta$ =1/4. Then the Maier-Meier equations can be represented in the form:

$$\varepsilon'_{\text{II}} = 1 + \frac{NHF}{\varepsilon_0}\left\{\gamma_{av} + \frac{2}{3}S\Delta\gamma + F\frac{p_e^2}{3k_BT}\left[1 - \frac{1}{4}S\right]\right\} \quad (5)$$

$$\varepsilon'_{\perp} = 1 + \frac{NHF}{\varepsilon_0}\left\{\gamma_{av} - \frac{1}{3}S\Delta\gamma + F\frac{p_e^2}{3k_BT}\left[1 + \frac{1}{8}S\right]\right\} \quad (6)$$

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Using (5-6) we obtain:

$$\Delta\varepsilon' = \frac{NHF}{\varepsilon_0}\left[\Delta\gamma - F\frac{p_e^2}{8k_BT}\right]S \qquad (7)$$

Let us denote by $\Delta S = S - S_0$, where S is the order parameter of the liquid crystal doped with nanotubes, S_0 is the order parameter of the pure LC; $\Delta\varepsilon'_{II}$ is the difference between the longitudinal component of the real part of the dielectric permittivity after doping and before doping of the liquid crystal; $\Delta\varepsilon'_\perp$ is the difference between the transverse component of the real part of the dielectric permittivity after and before doping of the liquid crystal; $\Delta(\Delta\varepsilon')$ is the difference between the dielectric anisotropy after and before doping the liquid crystal. Then you can write:

$$\varepsilon'_{II} = \frac{2NHF}{3\varepsilon_0}\left\{\Delta\gamma - F\frac{p_e^2}{8k_BT}\right\}\Delta S \qquad (8)$$

$$\varepsilon'_\perp = -\frac{NHF}{3\varepsilon_0}\left\{\Delta\gamma - F\frac{p_e^2}{8k_BT}\right\}\Delta S \qquad (9)$$

Their difference gives the change in dielectric anisotropy:

$$\Delta(\Delta\varepsilon')\frac{NHF}{\varepsilon_0}\left[\Delta\gamma - F\frac{p_e^2}{8k_BT}\right]\Delta S \qquad (10)$$

The experiment shows that the longitudinal and transverse components of the dielectric permittivity increase with the additive of SWCNs: $\Delta\varepsilon'_{II} > 0$ and $\Delta\varepsilon'_\perp > 0$. In addition, the dielectric anisotropy difference also increases, that is, $\Delta(\Delta\varepsilon') > 0$, although it decreases in absolute value. Obviously, the simultaneous implementation of conditions (8), (9) and (10) is impossible with these experimental results. Consequently, automatic use of the Maier-Meier theory for the analysis of the experimental results for the smectic LC with large dielectric anisotropy cannot be made. In addition, the possibility of interaction of the emerging dipole moments of nanotubes with the dipole moments of the liquid crystal, the direction of which has a certain angle with the long axis of the molecule, plays a certain role.

Frequency dependences of specific conductance of the pure LC and the colloid are shown inf fig. 3. As can be seen, the dispersion associated with the -C-NO$_2$ dipole fragment is also observed here. In this case, the additive of particles slightly increases the specific conductance up to this dispersion then it decreases. In particular, the longitudinal component increases from $1.72\cdot10^{-5}$ S/m to $2.45\cdot10^{-5}$ S/m and the transverse component changes from $9.92\cdot10^{-7}$ S/m to $1.80\cdot10^{-6}$ S/m at the frequency of 100 Hz. That is, the ratio $\sigma_{II}/\sigma_\perp$ is 17.3 for the pure LC while it becomes 13.6 for rhe colloid. The longitudinal component increases from $1.90\cdot10^{-1}$ S/m to $2.32\cdot10^{-1}$ S/m and the transverse component almost does not change and is equal to $1.42\cdot10^{-2}$ S/m at the frequency of 300 kHz. That is, the ratio $\sigma_{II}/\sigma_\perp$ in pure liquid crystal was 13.4 for the pure LC and becomes 16.3 when nanotubes are added.
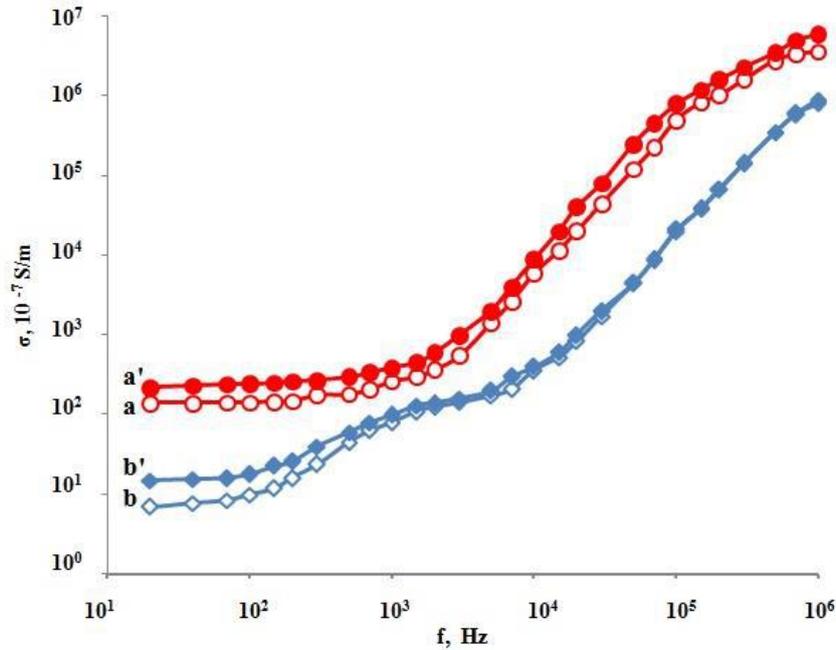
Fig.3. Frequency dependence of specific conductance components at 32^{0}C: (a) σ_{II} of the pure LC, (a') σ_{II} of the colloid, (b) $\sigma_\perp$ of the pure LC, (b') $\sigma_\perp$ of the colloid.

The increase in electric conductivity at low and medium frequencies is due to the percolation effect when nanotubes are added into the liquid crystal. A space set of conducting nanotubes is formed. In this case, there is predominance of electronic hopping conductivity over ionic conductivity. At high

frequencies, the molecules of the liquid crystal do not keep up with the changes in the direction of the electric field. Therefore, there is a sharp increase of conductivity at high frequencies. At the same time, the reversal of molecules in the colloid at application of electric field along the long axis of the molecules is hindered because of the increase of rotational viscosity relative to the pure LC. It is consistent with the increase in dielectric relaxation time.

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