

INFLUENCE OF SINGLE-WALLED CARBON NANOTUBES ON DIELECTRIC RELAXATION AND ELECTRIC CONDUCTIVITY OF SMECTIC A LIQUID CRYSTAL WITH POSITIVE DIELECTRIC ANISOTROPY

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The effect of single-walled carbon nanotubes (SWCNTs) on the dielectric and conductivity properties of smectic A liquid crystal 4- nitrophenyl -4'- decyloxybenzoic acid has been studied. It was shown that the additive of SWCNTs with concentration of 0.5% leads to a decrease in the order parameter of 5CB. In this case, the clearing point is raised, the longitudinal component of the dielectric permittivity decreases while the transverse component increases. The incipient percolation effect promotes to the dominance of hopping electron conductivity over ionic conductivity, leading to an increase in specific conductance.

Keywords: smectic A liquid crystal; single-walled carbon nanotubes, dielectric permittivity; electric conductivity

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1. INTRODUCTION

In recent years, an alternative direction in the chemistry and physics of liquid crystals (LC) has been the creation of hybrid liquid crystal systems in which liquid crystal mixes or comes into contact with some other structure without chemical interaction. In particular, all modern displays are based on hybrid liquid crystal systems in which field effects in liquid crystals are combined with the properties of thin-film structure. An example of a hybrid liquid crystal system is also a polymer dispersed by liquid crystal.

Single-walled carbon nanotubes (SWCNTs) are rod-shaped and have a diameter comparable to cross-section of elongated LC molecules. In addition, there is strong interaction of nanotubes with LC molecules, as a result of which they are aligned along the preferred direction (director) of LC molecules [1]. In that respect, liquid crystal with such nanoparticles can significantly change its physical properties. A very minute concentration of carbon nanotubes in liquid crystals can have an impact on their electrical and optical properties. Liquid crystals provide a distinctive medium for controlling the alignment of carbon whereas carbon nanotubes are important for the enhancement and fine-tuning of liquid crystalline properties [2].

One of the major applications of LCs is displays. Their operation is based on electro-optical effects in LCs, with which their dielectric and conductive properties are closely coupled. A set of works has been devoted to the study of the dielectric and electro-optic properties of LC doped with single-walled carbon nanotubes. It was shown in [3-4] that the inclusion of tiny amount (0.01-0.02 wt. %) of SWCNTs in the nematic matrix with positive dielectric anisotropy increases the nematic-isotropic transition temperature and dielectric anisotropy while threshold voltage decreases. Moreover, the composites filled in the cells have been probed under applied bias electric field and it enhanced the nematic ordering of the liquid crystal molecules in the composites which

results overall improvement of their dielectric and electro-optic parameters [4]. 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 work [5]. Influence of SWCNTs on the re-entrant phenomenon in LCs has been studied in [6]. 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. The presence of SWCNTs changes the physical properties like splay elastic constant, rotational viscosity and electrical conductivity. SWCNTs were dispersed in nematic liquid crystal 4-pentyl-4'-cyanobiphenyl at the concentration of 0.02 and 0.05 wt% in work [7, 8]. 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. Presence of SWCNTs increases the relaxation frequency corresponding to flip-flop motion of molecules around their short axes.

The aim of this work is to study the effect of SWCNTs at concentration corresponding to percolation phenomenon on the dielectric and conductivity properties of smectic A liquid crystal 4-nitrophenyl -4'- decyloxybenzoic acid .

2. MATERIALS AND METHODS

We used smectic A liquid crystal 4- nitrophenyl -4'- decyloxybenzoic acid as a matrix. A dielectric anisotropy of this LC is positive. The temperature range of smectic phase is located between 55°C and 77°C.

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 50°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.

Temperature of the smectic-isotropic transition was defined under the Carl Zeiss polarization microscope (model 720, Germany).

Dielectric and conductivity measurements were carried out by the Precision LCR Meter 1920 (IET Labs. Inc., USA) over the frequency range of 20 Hz – 1 MHz and at temperatures between 23°C – 43°C. In such a case, applied voltage was 0.5 V for both LC molecular orientations.

3. RESULTS AND DISCUSSION

Observations under the polarizing microscope showed that the clearing point decreases from 76.8°C to 75.1°C at the additive of single-walled carbon nanotubes into the liquid crystal. This is an indirect fact of a decrease in the order parameter of the liquid crystal.

The frequency dependences of the real and imaginary parts of the dielectric permittivity of both the pure LC and the corresponding colloid at the homeotropic configuration and temperature of 58°C are shown in Fig. 1.

As can be seen, the value of ϵ' for the colloid is less than for the pure liquid crystal at all frequencies. These values change slightly up to 10⁵ Hz then they decrease sharply. The value of ϵ' is 17.71 for the pure LC at the frequency of 2 kHz while it corresponds to 15.92 for the colloid. Starting from 9 kHz, the value of the dielectric permittivity of the colloid slightly increases and is 16.45 at 15 kHz. The presence of SWCNTs increases the value of ϵ'' to 30 kHz, then it is lower down to 1 MHz. In this case, the maximum of dielectric absorption is shifted to the high frequency region from 400 kHz to 600 kHz.

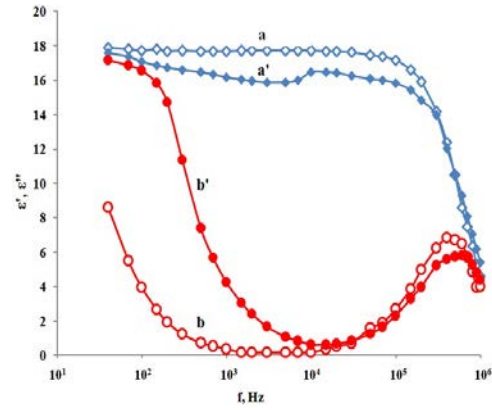


Fig. 1. Frequency dependences of the real ϵ' and imaginary ϵ'' components of the dielectric permittivity at the homeotropic configuration (temperature 58°C): (a) ϵ' of the pure LC, (a') ϵ' of the colloid, (b) ϵ'' of the pure LC, (b') ϵ'' of the colloid.

It is known that the relaxation time of LC molecules, which is characterized by the flip-flop motion of molecules from one direction to the opposite direction, is determined as follows:

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

where f is the frequency of the applied electric field. The addition of nanotubes reduces the relaxation time from $4.0 \cdot 10^{-7}$ s to $2.7 \cdot 10^{-7}$ s at 58°C. Obviously, this is due to a decrease in the connection between the LC molecules.

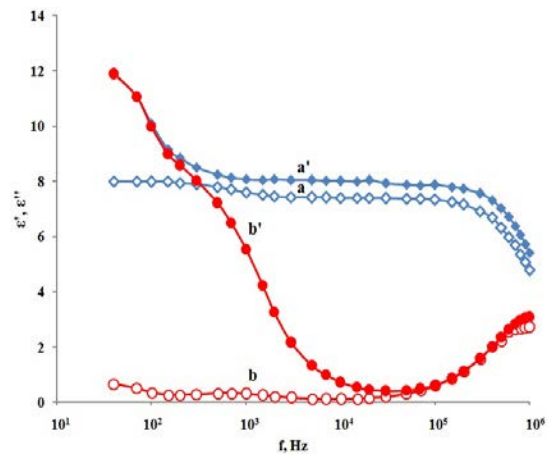


Fig. 2. Frequency dependences of the real ϵ' and imaginary ϵ'' components of the dielectric permittivity in the planar configuration (temperature 58°C): (a) ϵ' of the pure LC, (a') ϵ' of the colloid, (b) ϵ'' of the pure LC, (b') ϵ'' of the colloid.

The frequency dependences of the real and imaginary components of the dielectric permittivity of the pure LC and the colloid at planar configuration and temperature of 58°C are shown in Fig. 2. As can be seen, the value of ϵ' for the colloid is greater than for the pure LC at all frequencies. The real part of the dielectric permittivity remains almost unchanged for the colloid and the pure LC at medium frequencies. In this case, its value is 7.45 for pure LC while it

corresponds to 8.06 for the colloid at 2 kHz. The value of ϵ' decreases sharply after 10^5 Hz.

It should be noted that the dielectric anisotropy of the pure LC is 10.26 at medium frequencies while this value is 7.86 for the colloid. In other words, the addition of SWCNTs decreases the dielectric anisotropy.

We will analyze the experimental facts using the Mayer-Meier theory for nematic liquid crystals, which, in a rough approximation, can be used for smectic liquid crystals. According to this theory, expressions for both components of the permittivity are determined as follows [9]:

$$\epsilon'_{||} = 1 + \frac{NHF}{\epsilon_0} \left\{ \gamma_{av} + \frac{2}{3} S \Delta\gamma + F \frac{p_e^2}{3k_B T} \left[1 - \frac{1}{2} (1 - 3 \cos^2 \beta) S \right] \right\} \quad (2)$$

$$\epsilon'_{\perp} = 1 + \frac{NHF}{\epsilon_0} \left\{ \gamma_{av} - \frac{1}{3} S \Delta\gamma + F \frac{p_e^2}{3k_B T} \left[1 + (1 - 3 \cos^2 \beta) S \right] \right\} \quad (3)$$

From where we get:

$$\Delta \epsilon' = \frac{NHF}{\epsilon_0} \left[\Delta\gamma - F \frac{p_e^2}{2k_B T} (1 - 3 \cos^2 \beta) \right] S \quad (4)$$

where F is reaction field factor, H is the cavity form factor, $\gamma_{av} = (\gamma_{||} + 2\gamma_{\perp})/3$ is the average value of polarizability of LC molecules, $\Delta\gamma = \gamma_{||} - \gamma_{\perp}$ 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 concentration of the colloid is very small, the number of embedded particles per unit volume is also small. That is, the number of LC molecules per unit volume N decreases insignificantly. This liquid crystal has a positive dielectric anisotropy. Hence, its dipole moment is directed along the long axis of the molecule as well as the direction of maximal polarizability. Therefore, the angle $\beta = 0$ and $\cos \beta = 1$. In this case, the Maier-Meier expressions are converted to the form:

$$\epsilon'_{||} = 1 + \frac{NHF}{\epsilon_0} \left\{ \gamma_{av} + \frac{2}{3} S \Delta\gamma + F \frac{p_e^2}{3k_B T} [1 + S] \right\} \quad (5)$$

$$\epsilon'_{\perp} = 1 + \frac{NHF}{\epsilon_0} \left\{ \gamma_{av} - \frac{1}{3} S \Delta\gamma - F \frac{p_e^2}{3k_B T} [2S - 1] \right\} \quad (6)$$

Using (5-6) may be obtained:

$$\Delta \epsilon' = \frac{NHF}{\epsilon_0} \left[\Delta\gamma + F \frac{p_e^2}{k_B T} \right] S \quad (7)$$

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; $\Delta \epsilon'_{||}$ is the difference between the longitudinal component of the real part of the dielectric permittivity after doping and before doping of the liquid crystal; $\Delta \epsilon'_{\perp}$ is the difference between the transverse component of the real part of the dielectric permittivity after and before doping of the liquid crystal; $\Delta(\Delta \epsilon')$ is the difference between the dielectric anisotropy after and before doping the liquid crystal. Then you can write:

$$\Delta \epsilon'_{||} = \frac{NHF}{3\epsilon_0} \left[2\Delta\gamma + \frac{p_e^2}{k_B T} \right] \Delta S \quad (8)$$

$$\Delta \epsilon'_{\perp} = -\frac{NHF}{3\epsilon_0} \left[\Delta\gamma + F \frac{2p_e^2}{k_B T} \right] \Delta S \quad (9)$$

Their difference gives the change in dielectric anisotropy:

$$\Delta(\Delta \epsilon') = \frac{NHF}{\epsilon_0} \frac{p_e^2}{k_B T} \Delta S \quad (10)$$

It is obvious that the expressions in parentheses of relations (8) and (9) have positive values. The experiment shows a decrease in the longitudinal component of the dielectric permittivity ($\Delta \epsilon'_{||} < 0$) and, accordingly, the condition $\Delta S < 0$ must be satisfied, that is, the order parameter decreases with the additive of nanotubes. The experiment also shows an increase in the transverse component of the permittivity with the addition of nanotubes, that is, $\Delta \epsilon'_{\perp} > 0$. Therefore, the condition $\Delta S < 0$ is satisfied, indicating on decrease in the order parameter. Similarly, a decrease in the dielectric anisotropy also indicates a decrease in the order parameter of the colloid relative to the corresponding parameter of the pure liquid crystal. The decrease in the order parameter can be explained by the fact that an appreciable part of the nanotubes are localized in the

gap between the layers of the smectic liquid crystal, since their diameter is about 1 nm while the width of the gap is 2 nm. In this case, the ordering of LC molecules in the layers is disrupted, leading to a decrease in the order parameter and the clearing temperature.

The frequency dependences of the specific conductance of the pure LC and the colloid are shown in Fig. 3. As can be seen from this figure, the longitudinal component of the conductivity of the pure LC is greater than the transverse component. Obviously, this is due to the easier movement of ions along the director of the liquid crystal. Another thing is in the colloid, in which the percolation effect occurs. In the case, the predominance of the hopping electronic conductivity over the ionic one. Electrons move along the long axis of the nanotubes. This has the strong effect on the change in conductivity when nanotubes are embedded in the liquid crystal. The transverse component of the conductivity increases much more strongly than the longitudinal component. In particular, the longitudinal component of the conductivity of the pure liquid crystal increases from $1.82 \cdot 10^{-8}$ S/m to $2.44 \cdot 10^{-7}$ S/m at 40 Hz and from $2.28 \cdot 10^{-8}$ S/m to $2.40 \cdot 10^{-7}$ S/m at 2 kHz. With further increase in frequency, the specific conductance rises sharply and after the frequency of 15 kHz they equalize and reach the value of $4.19 \cdot 10^{-4}$ S/m at 1 MHz. The transverse component of the specific conductance of the pure LC upon the inclusion of nanotubes increases from $1.45 \cdot 10^{-9}$ S/m to $3.80 \cdot 10^{-7}$ S/m at 40 Hz and from $1.69 \cdot 10^{-8}$ S/m to $4.20 \cdot 10^{-7}$ S/m at 2 kHz. Then the specific conductance rises sharply, they equalize after 50 kHz and reach the value of $2.08 \cdot 10^{-4}$ S/m at 1 MHz. Note that additional electrons arising due to the percolation effect are delayed at high frequencies. For this reason, the specific conductance of the colloid has the same value as that of pure LC.

It is obvious that the change in conductivity correlates with a change in the imaginary part of the dielectric permittivity and the frequency. Therefore, the conductivity increases with an increase in these parameters. Due to the difference in the frequency

ranges of the dispersion $\varepsilon''_{\parallel}$ и ε''_{\perp} , the maxima $\varepsilon''_{\parallel}$ and ε''_{\perp} , are observed at different frequencies and, accordingly, σ_{\parallel} and σ_{\perp} begin to increase at the same frequencies. The additive of nanotubes shifts the dispersion of the dielectric permittivity to the high-frequency region. In this case, the same shift occurs with the dispersion of the conductivity.

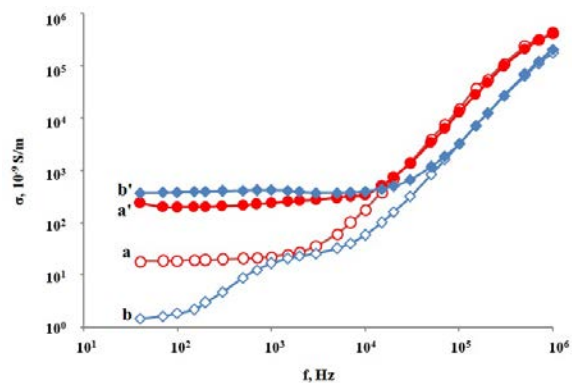


Fig. 3. Frequency dependence of the components of specific conductance at 58°C: (a) σ_{\parallel} of the pure LC, (a') σ_{\parallel} of the colloid, (b) σ_{\perp} of the pure LC, (b') σ_{\perp} of the colloid.

Ohmic conductivity in alternating current can be represented as:

$$\sigma = 2\pi f \varepsilon_0 \varepsilon'' \quad (11)$$

4. CONCLUSION

It is shown that the additive of single-walled carbon nanotubes into the smectic A liquid crystal with the concentration of 0.5 wt. % leads to a decrease in the order parameter and clearing temperature, which is connected with the inclusion of a part of the nanotubes into the gap between the layers. Due to the percolation effect, the electron hopping conductivity dominates over the ionic one, which leads to an increase in the specific conductance.

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