

Reduction of the order parameter and high electric conductivity of silver nanorods doped nematic liquid crystal

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Abstract

Influence of silver nanorods with concentration of 0.2 wt. % on dielectric and conductivity properties of nematic liquid crystal 4-cyano-4'-pentylbiphenyl (5CB) with positive dielectric anisotropy is investigated at the frequency range of 20 Hz - 1MHz and temperature 24°C. It is shown that the transverse component of the real part of dielectric permittivity increases at the additive of nanorods while the longitudinal component decreases. Accordingly, the dielectric anisotropy decreases. The image part of dielectric permittivity increases for both configurations of liquid crystal molecules at all investigated frequencies. In this case, a maximum of dielectric absorption shifts to the high-frequency region. This fact indicates on decreasing of relaxation time. Specific conductance increases sharply and for the transverse component to a greater extent than for the longitudinal one. An analysis of the experimental results based on the Maier-Meier theory indicates on a decrease in the order parameter with the additive of nanorods which is explained by the anchoring of the ends of the liquid crystal molecules with the surface of the nanorods. A sharp increase in conductivity is associated with the percolation effect in which the electron hopping conductivity dominates over the ionic one.

Keywords: nematic liquid crystal, silver nanorods, colloid, dielectric permittivity, conductivity.

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1. Introduction

Plasmonics has been attracting extensive attention across various fields. Since plasmon resonances are very sensitive to the surrounding environment of plasmonic nanostructures, varying dielectric properties of medium becomes effective way to have active control of the surface plasmon resonance. For this purpose, liquid crystals (LCs) stand out as an excellent candidates of active media since they possess dynamic, continuous, and most importantly, reversible tuning behavior using various driving strategies.

The aim of the report is to study of dielectric and conductivity properties of silver nanorods in liquid crystal 5CB.

2. Experiments

We used nematic liquid crystal (LC) 4-cyano-4'-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 21.3⁰C and 35.2⁰C.

The silver nanorods (US, Research were added into the liquid crystal with concentration of 0.2 wt. %. Then obtained mixture was shaken in a vortex mixer for 1 hour at temperature 80⁰C, 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 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).

Dielectric and conductivity measurements were carried out by the Precision LCR Meter 1920 (IET Labs. Inc., USA) over the frequency range of 20 Hz - 1MHz and at temperature 24⁰C. 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 different frequencies f . The magnitudes of dielectric permittivity ε were defined as:

$$\varepsilon = \frac{C}{C_0}, \quad (1)$$

where C_0 is the electric capacity of the empty cell. The real ε' part of dielectric permittivity up to 2 kHz was calculated by the expression

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

while for more frequencies, it was defined as follow

$$\varepsilon' = \frac{\varepsilon}{\sqrt{1 + D^2}} \quad (3)$$

Imaginary ε'' part of dielectric permittivity and electric conductance σ were calculated by the expressions:

$$\varepsilon'' = \varepsilon' D, \quad (4)$$

$$\sigma = 2\pi f \varepsilon_0 \varepsilon'' \quad (5)$$

3. Results and discussion

Figures 1 and 2 show the frequency dependence of real ε' and imaginary ε'' parts of dielectric permittivity of both the pure LC and the colloid for homeotropic and planar alignments, correspondingly, at temperature of 24⁰C.

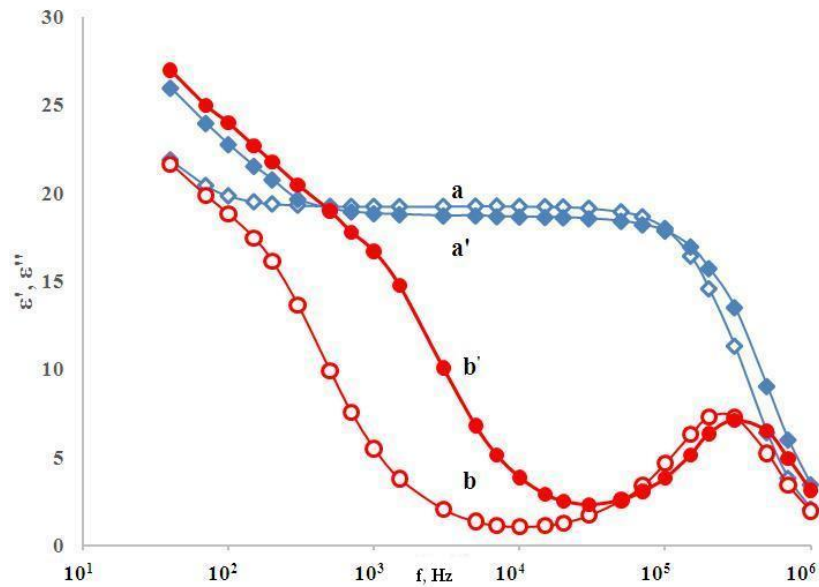


Figure 1. Frequency dependence of real ϵ' and imaginary ϵ'' parts of dielectric permittivity at homeotropic configuration (temperature 24°C): (a) ϵ' of the pure LC, (a') ϵ' of the colloid, (b) ϵ'' of the pure LC, (b') ϵ'' of the colloid

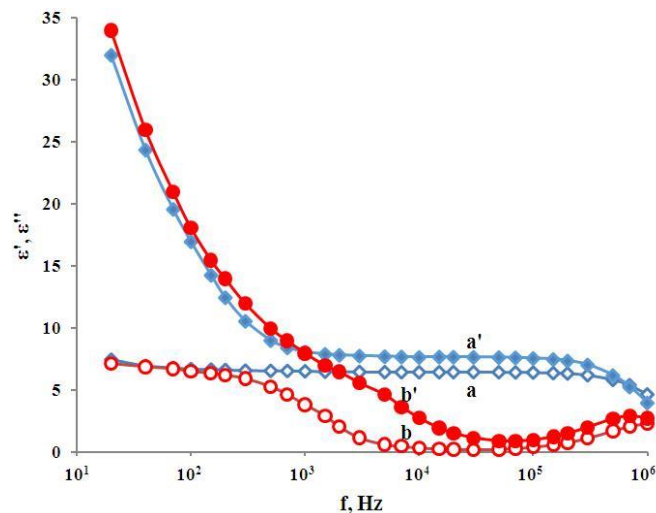


Figure 2. Frequency dependence of real ϵ' and imaginary ϵ'' parts of dielectric permittivity at planar configuration (temperature 24°C): (a) ϵ' of the pure LC, (a') ϵ' of the colloid, (b) ϵ'' of the pure LC, (b') ϵ'' of the colloid

The frequency dependence of ϵ' can be divided into three ranges. At low frequencies, an increase in dielectric permittivity occurs, which is associated with electronic exchange between electrodes and ions [1]. In the middle frequency region, the dielectric permittivity remains almost unchanged and is connected with the bulk properties of the sample. And finally, relaxation of the liquid crystal and the colloid starts in the high-frequency range. As is seen from indicated figures, the additive of nanorods decreases the longitudinal component of real part ϵ' of dielectric permittivity while it increases the transverse component in the middle frequency range.

The observable changes of dielectric permittivity can be explained by the Maier-Meier

theory for nematic LCs according to which expressions for components of dielectric permittivity are defined as follows [2]:

$$\varepsilon'_{||} = 1 + \frac{NHF}{\varepsilon_0} \left\{ \gamma_{av} + \frac{2}{3} S \Delta\gamma + F \frac{P_e^2}{3k_B T} \left[1 - (1 - 3 \cos^2 \beta) S \right] \right\} \quad (6)$$

$$\varepsilon'_{\perp} = 1 + \frac{NHF}{\varepsilon_0} \left\{ \gamma_{av} - \frac{1}{3} S \Delta\gamma + F \frac{P_e^2}{3k_B T} \left[1 + \frac{1}{2} (1 - 3 \cos^2 \beta) S \right] \right\} \quad (7)$$

$$\Delta\varepsilon' = \frac{NHF}{\varepsilon_0} \left[\Delta\gamma - F \frac{P_e^2}{2k_B T} (1 - 3 \cos^2 \beta) \right] S \quad (8)$$

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 an angle between the point molecular dipole and the axis of maximum molecular polarizability, ε_0 is dielectric permittivity of vacuum, k_B is Boltzmann constant, T is Kelvin temperature. Liquid crystal 5CB has positive dielectric anisotropy. 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:

$$\varepsilon'_{||} = 1 + \frac{NHF}{\varepsilon_0} \left\{ \gamma_{av} + \frac{2}{3} S \Delta\gamma + F \frac{P_e^2}{3k_B T} [1 + 2S] \right\} \quad (9)$$

$$\varepsilon'_{\perp} = 1 + \frac{NHF}{\varepsilon_0} \left\{ \gamma_{av} - \frac{1}{3} S \Delta\gamma - F \frac{P_e^2}{3k_B T} [S - 1] \right\} \quad (10)$$

Dielectric anisotropy is the difference of these quantities:

$$\Delta\varepsilon' = \frac{NHF}{\varepsilon_0} \left[\Delta\gamma + F \frac{P_e^2}{k_B T} \right] S \quad (11)$$

Let us denote by $\Delta S = S - S_0$, where S is the order parameter of the liquid crystal doped with nanorods, S_0 is the order parameter of the pure LC; $\Delta\varepsilon'_{||}$ is the difference between the longitudinal component of the real part of the dielectric permittivity after 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 we can write:

$$\Delta\varepsilon'_{||} = \frac{2NHF}{3\varepsilon_0} \left[\Delta\gamma + F \frac{P_e^2}{k_B T} \right] \Delta S \quad (12)$$

$$\Delta\varepsilon'_{\perp} = -\frac{NHF}{3\varepsilon_0} \left[\Delta\gamma + F \frac{P_e^2}{k_B T} \right] \Delta S \quad (13)$$

Using (12-13) may be obtained:

$$\Delta(\Delta\varepsilon') = \frac{NHF}{\varepsilon_0} \left[\Delta\gamma + F \frac{p_e^2}{k_B T} \right] \Delta S \quad (14)$$

It is obvious that the expressions in parentheses of formulae (12), (13) and (14) have positive values. The experiment shows a decrease in the longitudinal component of the dielectric permittivity ($\Delta\varepsilon'_{||} < 0$) and, accordingly, the condition $\Delta S < 0$ must be satisfied, that is, the order parameter decreases with the additive of nanorods. The experiment also shows an increase in the transverse component of the permittivity with the additive of nanorods, that is, $\Delta\varepsilon'_{\perp} > 0$. Therefore, the condition $\Delta S < 0$ is satisfied, indicating on decreasing in the order parameter. Similarly, a decrease in the dielectric anisotropy also indicates on a decrease in the order parameter of the colloid relative to the corresponding parameter of the pure liquid crystal. This fact may be explained by the anchoring of the ends of the liquid crystal molecules with the surface of the nanorods.

The frequency dependences of the specific conductance of the pure LC and the colloid are shown in Figure 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 situation takes place for the colloid, in which the percolation effect occurs. In this case, there is the predominance of the hopping electronic conductivity over the ionic one. Electrons move along the long axis of the nanorods. This has the strong effect on the change in conductivity when nanorods are embedded in the liquid crystal. The transverse component of the conductivity increases much more strongly than the longitudinal component.

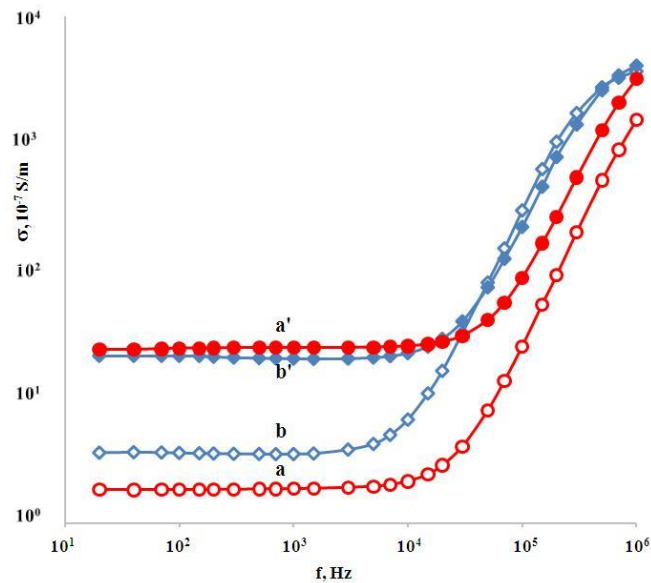


Figure 3. Frequency dependence of specific conductance components at temperature 24°C: (a) $\sigma_{||}$ of the pure LC, (a') $\sigma_{||}$ of the colloid, (b) σ_{\perp} of the pure LC, (b') σ_{\perp} of the colloid

At high frequencies, conductivity is stipulated by dielectric losses, that is, energy dissipation in the range of the Debye relaxation of the dipoles of LC molecules [3]. It is defined by the expression (5). It is obvious that the change of conductivity is correlated with the change of the imaginary part of dielectric permittivity and the frequency. Therefore, the specific conductance increases at increasing of indicated parameters.

4. Conclusion

It is shown that the dielectric anisotropy at the additive of silver nanorods in liquid crystal 5CB decreases indicating on a decrease in the order parameter connected with the anchoring of the ends of the liquid crystal molecules with the surface of the nanorods. The imaginary part of dielectric permittivity increases for both configurations of liquid crystal molecules at all investigated frequencies. In this case, a maximum of dielectric absorption shifts to the high-frequency region. This fact indicates on decreasing of relaxation time. Specific conductance increases sharply and for the transverse component to a greater extent than for the longitudinal one. A sharp increase in conductivity is associated with the percolation effect in which the electron hopping conductivity dominates over the ionic one.

References

1. H.Y. Chen, W. Lee.” *Appl. Phys. Lett.* 88 **22** (2006) 222105-1-3.
2. W. Maier, G. Meier, *J. Z. Naturforsch A* **16** (1961) 262.
3. Blinov, L, New York: Springer, 2011.