Liquid crystal ferroelectric colloids: non-synthetic method of adjusting properties

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Abstract

We found dramatic changes of the properties of LCs by dispersing ferroelectric nanoparticles. Specifically, ferroparticles greatly increase the nematic-isotropic transition temperature, birefringence and dielectric anisotropy of the LC. Ferroelectric nanoparticles/LCs colloids offer a simple and effective means to precisely control the physical properties of LC materials and optimize them for display applications.

1. Introduction

Liquid crystals with composites have attracted much attention in the last decades because of their unique electro- and magneto-optics and display applications [1].

The inclusions in known composite LC systems such as polymer-dispersed liquid crystals [2], suspensions of aerosil in LC matrices [3], produce director distortions that extend over macroscopic scales. As a result, the composites scatter a light strongly and look very different from homogeneous LC matrixes.

Recently we have proposed another approach for development of LC composites that is based on the idea of controlling properties of the LCs by adding of a low concentration of nanoparticles in a LC matrix [4-8]. We found that diluted LC colloids made from ferroelectric nanoparticles (volume fraction $c_{part} \leq 1\%$) possess fascinating properties. The nanoparticles do not disturb the LC orientation but despite insignificant concentration strongly modify the basic properties of the LC matrix. In particular, we observed that embedding submicron ferroelectric particles of $Sn_2P_2S_6$ in a nematic matrix caused a strong increase of the dielectric anisotropy (more than in 2 times), decrease of the Friederikcsz transition voltage and acceleration of the director reorientation in the electric field. Also, the colloid responded linearly to the electric field, i.e. the direction of the LC reorientation was determined by the sign of the applied electric field that is unusual for nematics. Our subsequent studies showed that particles from other ferroelectric materials (e.g. and $BaTiO_3$) in different nematic hosts also exhibit enhanced dielectric response and other physical properties of nematic matrix. Moreover, we have recently observed a giant increase the nematic-isotropic transition temperature T_c of almost 40°C in the LC mixture MLC-6609 at its doping with nanoparticles $BaTiO_3$ in very light concentration $c_{part} \approx 0.2\%$ [8]. We found that the giant increase of T_c is caused by increase of the order parameter of LC matrix due to a strong electric field around ferroelectric particle. This electric field appears do to a huge steady dipole moment and high dielectric constant of the ferroelectric particle. Increase of the order parameter should result in increase of the values of all basic LC parameters, which depends on the order parameter and determine main electro-optical characteristics of LC devices (birefringence, dielectric anisotropy, Frank constants, etc). Thus, by addition of a small quantity of ferroparticles to LCs, we can effectively tune the basic properties of LC materials. Below we illustrate this idea on examples of the control of birefringence and dielectric anisotropy of commercial LC materials by their doping with ferroelectric nanoparticles

2. Materials and experiment

For our investigations we have used several kind of LCs from Merck for different applications: MLC-6609 (T_c = 91.5°C, birefringence n_a = 0.077, dielectric anisotropy, ε_a = -2.4) for vertical alignment mode, LC 18523 (T_c = 55°C, n_a = 0.049, ε_a = 2.4) for telecomunication application and ZLI -4792 (T_c = 91°C, optical anisotropy n_a = 0.097, ε_a = 5.2) for active matrix TN LCDs. We also used model LC 5CB in some experiments. These LCs were doped with ferroelectric particles $BaTiO_3$ from Aldrich. Size of the particles as was confirmed by TEM-pictures was about 50 nm. The spontaneous polarization of a monocrystal of $BaTiO_3$, P = 26 μC/cm^2 [9]. We also used ferroelectric nano-particles of $St_2P_2S_6$, which spontaneous polarization, P = 14 μC/cm^2 [4]. The detailed preparation process of the colloid was analogous to that was described in our publication [4].

Temperatures of the nematic-isotropic transitions, T_c, were measured by DSC technique as well as by observation of the LC textures in polarizing microscope. The temperature of the cells was controlled with hot stage within 0.05°C accuracy.

Dielectric anisotropy, $\varepsilon_a(T)$, was measured at a frequency f=10^3 Hz with standard auto balancing bridge method. The experimental set-up was calibrated by the prior measurements of the empty cells. The temperature of the cells was controlled with hot stage within 0.01°C accuracy.

Birefringence $n_a(T)$ was determined by measuring the phase shift between e- and o-waves $\varphi = \pi d n_a / \lambda$ in the planar cells. Some experiments were carried out with Abbe refractometer.

3. Results and discussion

Birefringence. Considering the ferroelectric nanoparticles as effective molecular dopant, one can write the expression for the gain of the birefringence with respect to the pure LC as [8]

$$\frac{n_a^{col}}{n_a^{LC}} = \frac{\left(n_e^{LC} + n_0^{LC}\right)}{\left(n_e^{col} + n_o^{col}\right)} \frac{\bar{\gamma}_a^{col}}{\gamma_a^{LC}} \frac{S_{col}}{S_{LC}}, \qquad (1)$$

where $\bar{\gamma}_a^{col} = \left(1 - c_{part}\right)\gamma_a^{LC} + c_{part}\left(\gamma_a^{part}\right)$, γ_a^{LC} is the anisotropy of polarizability of LC molecules, γ_a^{part} is the anisotropy of polarizability of ferroelectric particles. As was shown in [8], the

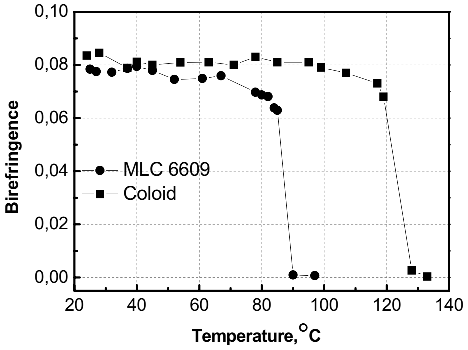

Figure 1. Temperature dependences of the birefringence of MLC-6609 and the ferroelectric colloid ($c_{part} \approx 0.2\%$).

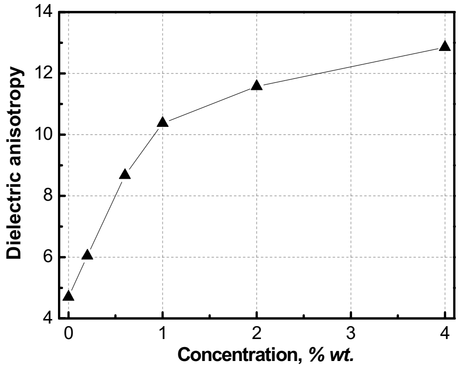

Figure 2. Concentration dependences of the dielectric anisotropy of the ferroelectric colloids (ZLI 4801+$Sn_2P_2S_6$).

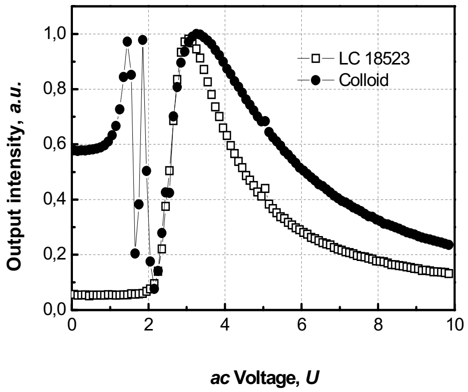

Figure 3. Dependence of transmittance of pure LC 18523 and ferroelectric colloid on applied field (*f=1kHz*).

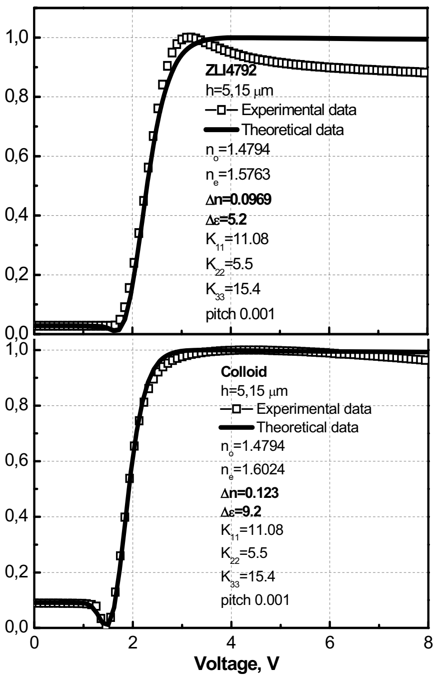

Figure 4. The experimental and simulation datas of LC electro-optic characteristics.

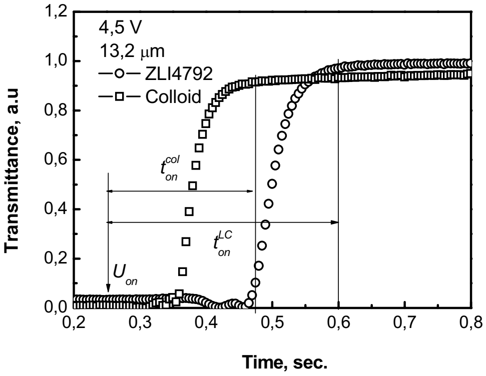

Figure 5. Turn-on time of the pure ZLI 4792 and ferrocolloid.

ratio (1) is determined in the main by the factor S_{col}/S_{LC}. Therefore, one can expect a gain of the birefringence in the colloid proportional to the increase of the order parameter of LC due to the nanoparticles. As an example, the temperature dependencies $n_a^{col}(T)$ and $n_a^{LC}(T)$ for LC MLC-6609 and nanoparticles BaTiO$_3$ is presented in Figure 1. The gain of the birefringence is 10% at room temperature. Since the temperature dependencies $n_a^{col,LC}(T)$ are determined by the dependencies $S(T)$, this value increases with approaching to the temperature T_c .We also observed the increase n_a^{col} with the increase of the volume fraction, c_{part}.

Dielectric anisotropy. The dielectric anisotropy of the colloid of ferroelectric nanoparticles in a LC matrix is determined by the order parameter of the matrix and dielectric properties of the colloid components. If the gain of the dielectric anisotropy is basically determined by the increase of the nematic ordering, we should observe the gain of the dielectric anisotropy at low frequency (i.e. ν = 1 kHz) in the colloid $\varepsilon_a^{col}/\varepsilon_a^{LC}$ close to the ratio $\varepsilon_a^{col}/\varepsilon_a^{LC} = \left(n_a^{col}\right)^2/\left(n_a^{LC}\right)^2 \approx S_{col}^2/S_{LC}^2$ at optical frequency. Direct contribution of the dielectric constant of the nanoparticles in the effective dielectric constant of the colloid give additional positive input to the gain of ε_a^{col} [5,10]. We found that for LC MLC-6609 $\varepsilon_a^{col}/\varepsilon_a^{LC}$ =1.54 at T = 32°C. One can see that this ration is close to $\left(n_a^{col}\right)^2/\left(n_a^{LC}\right)^2 \approx S_{col}^2/S_{LC}^2$ = 1.44. We suggest that the higher value $\varepsilon_a^{col}/\varepsilon_a^{LC}$ than $\left(n_a^{col}\right)^2/\left(n_a^{LC}\right)^2$ is due to a contribution of the high dielectric constant and the permanent polarization of the ferroelectric particles to the effective dielectric function of the colloid [10]. Increase of the dielectric anisotropy is 50% at room temperature and this value increases with approaching to the temperature T_c. The value ε_a^{col} also increases with the increase of the volume fraction of the nanoparticles, c_{part}. As example, the concentration dependences of the dielectric anisotropy of the ferroelectric colloid of Sn$_2$P$_2$S$_6$ in LC ZLI 4801is presented in Figure 2.

Fredeeriksz transition voltage. The threshold of the Fredeeriksz transition is determined by the expression

$$U_{th} \propto \sqrt{K/\varepsilon_a}\,, \qquad (2)$$

where K is a Franks constant. Since $\varepsilon_a^{col} \propto S$ and $K \propto S^2$, one can expect increase of the threshold of the Fredeeriksz transition in the colloid. At the same time, we have found more or less decreasing of the Fredeeriksz transition voltage in all studied colloids. As an example, the Fredeeriksz transition curves for pure LC 18523 and for the colloid is presented in Figure 3. This fact may be explained by an orientation torque in a LC matrix from the particles at their reorientation toward electric field [10].

Increased dielectric anisotropy and birefringence of the LC nano-colloids result in improvement of electro-optical characteristics of deferent LC modes. In Figure 4 the transmittance-voltage (TV) characteristics of 90° twist-cells with LC ZLI 4792 and colloid of Sn$_2$P$_2$S$_6$ ferroparticles in this LC. One can see that the optical retardation of the ZLI 4792 in the cell with the thickness L = 5 µm matches to the Maugine minimum ($T \approx 0$ at $U = 0$), and the cell with the colloid is out of the Maugine minimum ($T \neq 0$ at $U = 0$). It points at an increased birefringence of the colloid. We simulated the experimental TV-curves by using the software for electro-optics of TN-cells (Twist Cell Optics 6.0, LCI). We varied the values ε_a and n_a in this simulation to get the best fitting. In addition, we varied Frank constant for pure LC, keeping their ratio constant and equal to the values of the Merck catalogue [11]. The other actual parameters were fixed and their values are depicted in the plots. The best fitting for pure LC was obtained at the values ε_a^{LC} = 5.2 and n_a^{LC} = 0.097 (these values are close to the data [11]), and for the colloid we have obtained increased values ε_a^{col} = 9.2 and n_a^{col} = 0.123. Thus, the gain $n_a^{col}/n_a^{LC} \approx 1.28$ and the gain $\varepsilon_a^{col}/\varepsilon_a^{LC} \approx 1.77$.

Increased dielectric anisotropy of the colloid results in faster switching-on of the TN cell. In Figure 5 the switching on characteristics of the TN cells for ZLI 4792 and the colloid is presented. The time from the start of the voltage application to achievement of 90% of the maximum transition is 0.35 sec. for ZLI 4792 and 0.225 sec. for the colloid.

The comparative characteristics of the studied LC and colloids are summarized in the Table. The data is given for the weight concentration of the particles c_w = 1%.

	Increase n_a	Increase ε_a	*Increase T_c*, °C
ZLI-4792 + BaTiO$_3$	0,026 (~10%)	4.0 (~80%)	7.0
MLC-6609 + BaTiO$_3$	0.008 (~10%)	1.2 (~ 50%)	37.4
LC 18523 + BaTiO$_3$	0.045 (~80%)	2.2 (~ 50%)	13.2
ZLI-44801 + St$_2$P$_2$S$_6$	0,024 (~10%)	5.4 (~90%)	8.0
5CB + St$_2$P$_2$S$_6$	0,012 (~10%)	2.1 (~10%)	2.5

One can see that the smallest effect of the particles was observed in the LC 5CB. We connect this with the dimer structure of 5CB molecules in the mesophase.

4. Conclusion

Our results clearly show the unique properties of ferroelectric nanoparticles/LC colloids. The huge ferroelectric dipole moment of the nanoparticles produces a powerful field inducing dipolar intermolecular interactions that compete with the spontaneous intermolecular interaction. The additional interaction then leads to a dramatic increase in the LC mean field interaction and thence to a strong increase in order parameter of the LC matrix. This also causes the homogeneous ferroelectric LC colloid to have a higher birefringence, dielectric anisotropy and Frank constants than the pure LC material. These results are a general feature of colloids made from ferroelectric nano-particles dispersed in thermotropic liquid crystal matrices. As a result ferroelectric nanoparticles/LC colloids offer a simple and effective means to control the basic properties of liquid crystalline materials.

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