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Molecular Dynamics simulation and experimental investigation of material and structural parameters of multicomponent ferroelectric liquid crystal mixture

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Abstract

The influence of the conformation state of the chiral component on the spontaneous polarization ($P_s$) of multicomponent ferroelectric liquid crystal mixture was investigated using the molecular dynamics (MD) simulation method. It was demonstrated that the low-polarized conformational states of the chiral component was the most probable among all possible ones. The combination of the MD simulations and experimental measurements of liquid crystal mixture properties could be utilized to determine the conformation state of the chiral component dispersed in the ferroelectric liquid crystal mixture.

1. Introduction

Liquid crystals (LCs) are known due to their application in display technologies (LCDs), where they play the role of the light modulating media[1]. Most of the modern LC-based devices are based on nematic liquid crystals (NLCs). This type of LCs possesses the orientational ordering of anisomeric molecules but absence of the spatial ordering of their centers of gravity[2]. The electrooptic response time of NLC’s devices lays in millisecond range, which is the result of the elastic relaxation of the director. To enhance the performance of the devices, ferroelectric liquid crystals (FLCs) are proposed to utilized instead of NLCs. FLCs are chiral smectic C (SmC*) liquid crystals with 1D orientational and positional ordering. Due to their symmetry group ($C_2$), they have uncompensated macroscopic electric dipole moment (or spontaneous polarization-$P_s$)[3]. Coupling of the spontaneous polarization with external electric field leads to fast (microseconds range), polarity sensitive electrooptic response with in-plane switching of
effective optical axis as well as various electrooptic modes[4][5][6] which makes them perspective for emerging applications: color sequential active matrix liquid crystal displays (LCDs), bistable LCD, advanced spatial light modulators[7][8]. To meet the requirements imposed by the applications, the FLC must have wide temperature range of SmC* phase, low rotational viscosity, relatively high spontaneous polarization etc. Unfortunately, practically no one single compounds can satisfy such requirements. Therefore, it was proposed to employ multicomponent mixtures to solve this problem. Usually they consist of more than three different single compounds and such combination is enhancing and/or optimizing required parameter of the mixture. As the rule, to induce SmC* phase, a chiral compound is dissolve in the achiral matrix. In this case, the achiral matrix gives the main contribution to the rotational viscosity, whereas the chiral component induces the spontaneous polarization. Despite all successes in development of FLC’s and other liquid crystalline mixtures, it is not trivial to predict their properties in advance. Significant interest was attracted to the application of the Molecular Dynamics (MD) simulation approach [9], [10],[11] to predict the properties of the LCs. MD simulation method is widely used for investigation of structure and conformational movability of biopolymers[12] such as ribosome[13]. In the field of liquid crystals, MD simulation was utilized for investigation of material and thermodynamic properties of mesogenic compounds[14],[15],[16],[17],[18],[19] and mixtures[20],[21]. It was applied for prediction of ERP spectra of liquid crystal phase[22], investigation of organic dyes[23] and gases[24] distribution in nematic and smectic liquid crystals. Dielectric properties of ferroelectric discotic liquid crystal were also studied by molecular simulations[24]. MD simulations were used to investigate phase transitions in smectic liquid crystals[25].

The quantitative relationship between spontaneous polarization and the chirality index in the series of molecules with small systematic structural changes was previously reported[25]. These results point out the importance of conformational features, which determine the shape and flexibility of molecular fragments for mesogens properties related with polarization. Even more challenging can be the development of models that take into account the influence of molecular environment on the conformational flexibility of smectic C* mesogens.

This article is aimed to the Molecular Dynamics (MD) simulation of the influence of a chiral component’ conformational state of the ferroelectric liquid crystal (FLC) multicomponent
mixture CHS1 on its structural ordering, macroscopic electric dipole moment and dielectric permittivity. The results of the MD simulation will be compared with the experimental data.

2. Experimental

2.1 Ferroelectric liquid crystal mixture

For further investigations, the FLC mixture (acronym – CHS1) was designed following the strategy described in [26]. CHS1 (Fig.1) consists of achiral molecules of alkyl ethers of 2-(4-hydroxyphenyl)-5-(hydroxy)pyrimidines (LC1, LC2, LC3) and the non-mesogenic chiral component: p-bis-[4-(hex-2-yloxy carbonyl)-phenyl]benzene (LC4)[27].

The liquid crystal phase transition sequence of CHS1 (Cr-291K-SmC*-347K-SmA-357K-Iso) was measured with a differential scanning calorimeter Linkam DSC-600 and verified with the simultaneous observation of the liquid crystal texture transformations with a polarizing microscope Olympus BX51.

<table>
<thead>
<tr>
<th>Name</th>
<th>Mol fraction</th>
<th>% wt</th>
<th>Phase transition temperatures, K</th>
<th>Molecular structure</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>T_{cr-pat-SmC}</td>
<td>T_{SmC-SmA}</td>
<td>T_{SmA-N}</td>
<td>T_{N-I}</td>
</tr>
<tr>
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<td>3</td>
<td>26.6</td>
<td>340.95</td>
<td>387.95</td>
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<td>LC2</td>
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<td>24</td>
<td>348.15</td>
<td>387.15</td>
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<tr>
<td>LC3</td>
<td>3</td>
<td>32.9</td>
<td>341.95</td>
<td>396.85</td>
</tr>
<tr>
<td>LC4</td>
<td>1</td>
<td>16.5</td>
<td></td>
<td>377.15</td>
</tr>
</tbody>
</table>

Figure 1. Components of ferroelectric liquid crystal mixture CHS1
The smectic layer thickness was measured with X-ray diffractometer (Stoe) as the function of temperature (Fig. 2a). At room temperature (298 K), it is equal to around 28.378 Å.

2.2 Circular dichroism spectrum

The circular dichroism (CD) spectrum of the FLC mixture confined in a cell with homeotropic alignment was measured with a Jasco J810-S CD spectrometer in the spectral range 200–1000 nm at room temperature (T≈300 K)[28]. The measured CD spectrum was defined in terms of the ellipticity θ (Fig. 2b):

\[
\tan \theta = \frac{\sqrt{I_R} - \sqrt{I_L}}{\sqrt{I_R} + \sqrt{I_L}}.
\]  

(1)

Here \(I_R\) and \(I_L\) are intensities of the transmitted right- and left-handed circularly polarized light. Owing to the homeotropic alignment of FLC, the contribution of the FLC birefringence, linear dichroism, as well as turbidity to the CD measurements could be neglected. The CD spectrum of the pristine FLC has only one negative band centered at \(\lambda \approx 335\) nm outside the chromophoric absorption bands.

Figure 2. a) Dependence of the smectic layer thickness on temperature; b) CD spectrum of CHS1
Hence it cannot be explained by the exciton coupling mechanism. However, this band can be interpreted in frame of the intermolecular chirality transfer from the orientationally ordered chiral compound to the achiral host due to the core-core interaction leading to the host matrix chiralization. The measurement of the CD spectrum allowed to estimate the helical pitch of the mixture, which is equal to \( p \approx 510 \text{ nm} \) (\( T = 298 \text{ K} \)).

### 2.3 Electrooptic measurements

For the investigation of the FLC mixture, the cell (cell gap-\( d \approx 2.7 \times 10^{-6} \text{ m} \), active area \( S = 1.2 \times 10^{-4} \text{ m}^2 \)) consisted of two glass plates with conductive indium tin oxide (ITO) electrodes and unidirectionally rubbed polymer layers (Nylon 6) providing the planar alignment was utilized. The electroooptic characteristics of the cells were measured with the setup consisting of a He-Ne laser (\( \lambda = 632.8 \text{ nm} \)), a frequency generator (HP 33120A), a voltage amplifier (FLC Electronics, FLC20A), a digital oscilloscope (Tektronix 1002B), a p-i-n photodiode (Thorlabs), a computer-driven rotating table and a temperature controlled stage (Linkam, LTS-420).

To measure the response time (\( \tau \)) and the tilt angle (\( \theta \)), a bipolar rectangular wave voltage [29] with amplitude \( V = 10 \text{ V} \) and frequency \( f = 10 \text{ Hz} \) was applied to the cells. For measurement of the spontaneous polarization (\( P_s \)), the current reversal technique was utilized [29]. The material parameters (\( P_s, \tau, \theta \)) were measured in the temperature range of the SmC* phase of the CHS1 mixture[30]. The tilt angle and the spontaneous polarization are equal to 22.5° and 42 nC/cm² (at room temperature), respectively.

### 2.4 Dielectric measurements

The complex impedance spectrum (\( Z = Z' - iZ'' \)) of the cell was measured with the impedance spectrometer (Beta System, Novocontrol) in frequency range (\( f \)) 1 mHz-250 kHz at temperature \( T = 300 \text{ K} \) within the SmC* phase. The amplitude of the applied oscillating signal (\( V = 0.1 \text{ V} \)) is close to the thermal voltage (\( k_B T/e \approx 2.7 \times 10^{-2} \text{ V} \), \( T = 300 \text{ K} \), \( e \) - the elementary charge, \( k_B \) - the Boltzmann constant). Hence, we can assume that the external probing field is weak enough and does not influence the spatial charge distribution inside the cells as well as does not switch the FLC molecules due to the coupling with the spontaneous polarization vector. As result, one can consider that the investigated FLC cells have linear dielectric response and the nonlinear
effects can be excluded from the further analysis. We can also suppose that the applied probing voltage drops completely on a FLC layer but on the other components of a cell. The real ($\varepsilon'$) and imaginary ($\varepsilon''$) parts of the permittivity were derived from the impedance spectra using relations:

$$\varepsilon' = \frac{Z''d_{cell}}{2\pi f \varepsilon_0 s(Z'^2 + Z'^2)}$$  \hspace{1cm} (2)$$

and

$$\varepsilon'' = \frac{Z'd_{cell}}{2\pi f \varepsilon_0 s(Z'^2 + Z'^2)}.$$  \hspace{1cm} (3)$$

Here $\varepsilon_0$ is the dielectric permittivity of vacuum ($\varepsilon_0 = 0.885 \times 10^{-11}$ F/m). The experimentally measured real and imaginary parts of the dielectric spectra of the samples as well as the Cole-Cole diagrams are shown in Macdonald plots (Fig.3). The measured dielectric spectra were fitted with the equation:

$$\varepsilon = \varepsilon' - i\varepsilon'' = \varepsilon'(\infty) + \sum_j \Delta\varepsilon_j / (1 + (i2\pi f\tau_j)^{\beta_j}) + \sigma_{DC}/i2\pi \varepsilon_0 f,$$  \hspace{1cm} (4)$$

using the complex nonlinear least squares (CNLS) method based on the Levenberg-Marquardt minimization algorithm. Here $\varepsilon'(\infty)$ is the relative permittivity at the high frequency limit, $\Delta\varepsilon_j$ is the dielectric strength of the jth characteristic relaxation mode. The relaxation time of the jth mode

**Figure 3.** a) Complex dielectric spectrum of CHS1(filled black squares – real part of spectrum, filled blue circles- imaginary part of spectrum); b) Cole-Cole plot. T=300 K
is $\tau_j$; $\beta_j$ is the distribution parameter. The last term ($\sigma_{DC}/i2\pi\epsilon_0 f$) describes contribution of the ionic conductance. The contributions of the ITO resistance and the lead induction to the total impedance were neglected. From the fitting of the experimental data one the parameters and nature of the relaxation modes were identified. In the low frequency range (<100 Hz), the dielectric response is dominated by the ionic conductivity and the interfacial polarization[31]. In the middle frequency range (100 Hz $< f < 10^5$ Hz), the main contribution to the complex dielectric spectra comes from the Goldstone and soft modes. High frequency range is dominated by the electronic polarization of the FLC. As follows from the fitting the high frequency permittivity ($\epsilon'(\infty)$) is equal to around 1.98.

3 Molecular Dynamics simulation

Components of the liquid-crystal phase were modeled using GAFF force field[32]. Optimized molecular structures and its molecular electrostatic potentials were obtained by quantum-chemical Hartree-Fock calculations with the 6-31G* basis set. Partial charges were evaluated with the RESP model[33].

All MD simulations and analysis of the obtained trajectories were carried out using the GROMACS[34] software version 5.1.4. The integration time step was 2 fs in all simulations, the coordinates were recorded into the trajectory file every 25 ps. The LINCS algorithm[35] was used to limit lengths of bonds with hydrogen atoms. The simulation was run at a temperature of 298.15 K with 0.1 ps coupling time controlled by a velocity rescaling thermostat with additional stochastic correction[36] and periodic boundary conditions at an anisotropic constant pressure controlled by a Berendsen barostat[37] with 0.5 ps coupling time and zero compressibilities along tangential stresses. Particle mesh Ewald algorithm with 0.125 nm grid spacing and the fourth order interpolation was applied to the both types of electrostatic [38] and van der Waals [39] interactions.

Computation of bias exchange well-tempered metadynamics [20,21] of the LC4 chiral component was performed with the PLUMED software version 2.3 [41] working in conjunction with GROMACS software version 5.1.4. The biasing potential was adjusted by addition of Gaussians with 3 kJ/mol height and 10 degree width every 2500 steps (5 ps) until the Gaussian height reached approximately 0.001 kJ/mol. The bias factor was 10. The simulation used eight
replicas, the weighing potential of each of which depended on one of the torsion angles describing the conformation of the LC4 chiral component (Fig. 4).

Figure 4. Torsion angles describing conformation of the LC4 chiral component

3.1 Principles of minimum cell construction

The aggregate model of the liquid-crystal phase was constructed as an assembly of identical minimal cells. The minimal cell contained the minimum possible quantity of component molecules: one molecule of the LC4 chiral component, three molecules of the LC1 and LC3 achiral components each, and two molecules of the LC2 achiral component. Since the liquid-crystal phase should not have inherent dipole moment in the absence of an external electric field, the following conditions were applied: the total dipole moment and the projection of the dipole moment on the Ox axis of the minimum cell was to be minimal. In total, 36 combinations of achiral component orientations, characterized by a minimum dipole moment, were found. A minimal orthorhombic cell was constructed for each of them, in which the components in the most "unfolded" conformations were randomly arranged along the $3 \times 3 \times 1$ grid so that the long axis of the molecule was oriented along the $Ox$ axis. (Fig. 5b).
Figure 5. a) Molecular dipole moment direction for the achiral component; b) the mutual alignment of the liquid-crystal mixture components in a minimal cell.

Optimization of conformations and positions of molecules with the steepest descent method, 2 ns MD simulation at a constant volume and 20 ns MD simulation at an anisotropic constant pressure were consequently performed for each minimal cell. In the latter case simulated annealing was performed, in which the temperature varied with time (Fig. 1S–Supplementary information), what was used to better equilibrate the system. In the last 10 ns of those trajectories the polarizations of the cells were calculated. The cell, in the best way reproducing the absence of polarization in the studied liquid-crystal phase, was selected. The state of the selected cell obtained by these calculations was used in calculation of the bias exchange well-tempered metadynamics. During that process each 8 trajectories with duration of 77 ns were obtained.

3.2 Low- and high-polarized states of liquid-crystal mixture

The two types of minimal cell packing, with the high-polarized conformer of the chiral component (HPCC) and the low-polarized conformer of the chiral component (LPCC), were selected from the obtained set of minimal cells by the GROMOS [12] clustering method to construct liquid-crystal phases with high (HPP) and low (LPP) polarization, $P$, respectively. We assumed that the torsion angle values for stable LC4 conformers in the modeled phase were to take values close to those corresponding to the minima of the free energy $\Delta G_\phi$. With this condition, the array of states of the minimal cell obtained during the calculation of metadynamics was divided into parts in such a way that only one of the LC4 chiral component conformers was found in each of them. Then the states, isolated in each of those parts, were clustered according to coordinates of all atoms of the minimal cell excepting the H atoms. The number of the most energetically favorable packing of molecules in the minimal cell found by that operation was 64. Each of them corresponded to specific conformation of the LC4 chiral component. Herewith we have been guided by the following conditions. Firstly, the LPCC minimal cell is to have the minimal free energy $\Delta G_{\text{cell}}$, i.e. it is to be the most stable:

$$\Delta G_{\text{cell}} = \sum_{i=1}^{8} \Delta G_{\phi_i}$$

(5)
where \( \Delta G_\varphi \) is measured from the least deep minimum, in which it is taken as zero, so that for deeper minima \( \Delta G_\varphi \) is negative. Secondly, HPCC is to produce a minimal cell with a larger polarization than a minimal cell produced by LPCC. Thirdly, the LPCC minimal cell is to come over to the HPCC minimal cell along the shortest path, for example, on change of one torsion angle of the chiral component. Fourthly, this transition is to correspond to the lowest possible energy barrier, since with the growth of the energy barrier the time of the transition through it grows exponentially.

Each phase fragment was assembled from \( 2 \times 3 \times 5 \) minimal cells of the corresponding type, so that each simulated system contained 270 molecules. For both HPP and LPP fragments the conformations and positions of molecules were optimized by the steepest descent method, followed by the calculation of 400 ns equilibrium MD at an anisotropic constant pressure. When performing the latter calculation, torsion angles determining the conformation of the LC4 chiral component were limited by parabolic restraints with the 100 kJ/mol force constant in order to exclude spontaneous conformational transitions.

### 3.3 Analysis of trajectories

Analysis of the trajectories obtained for fragments of HPP and LPP included calculation of polarizations, \( P \), of phase fragments and contributions of individual components, calculation of the angle of deviation of the molecule main axis from the director (\( Ox \) was selected), \( \alpha \), and the nematic order parameter, \( S' \):

\[
S' = \frac{1}{2}(3\cos^2(\alpha) - 1); \tag{6}
\]

the angles of orientation of the main axes of the molecules \( \varphi \) and \( \Theta \) in polar coordinates, their joint probability distribution \( P(\varphi, \Theta) \), entropy \( S \):

\[
S = -P(\varphi, \Theta) \ln P(\varphi, \Theta); \tag{7}
\]

and potential of mean force (PMF), expressed in \( k_B T \), were also calculated:
\[ PMF = - \ln P(\varphi, \Theta) \] (8)

The latter value was used to describe the orientations of the main axes of the components of the liquid-crystal phases. All those values were calculated for trajectory sections from 200 to 400 ns.

4 Discussion

4.1 MD simulation of low- and high-polarized liquid-crystal phases

The dipole moments of the achiral components, LC1, LC2, LC3, are directed along the long axes of the molecules from the benzene to the pyrimidine ring (Fig. 5a), whereas the dipole moment of the LC4 chiral component, is directed perpendicular to the long axis of the molecule, and its value significantly depends on the LC4 conformation (Table 3S – Supplementary information). The conformation of LC4 chiral component is determined by three types of intramolecular rotations (Fig. 4). Firstly, these are rotations of the carbonyl groups from the both sides of terphenyl fragment; they are described by the \( \varphi_1 \) and \( \varphi_2 \) torsion angles. Secondly, these are rotations of sec-hexyl groups around ester bonds, described by \( \varphi_5 \) and \( \varphi_6 \) torsion angles. Thirdly, these are rotations of the phenyl groups relative to each other in the terphenyl fragment, described by the \( \varphi_3 \) and \( \varphi_4 \) torsion angles. Rotations around both bonds between the carbonyl carbon atoms and the ester oxygen atoms are described by the \( \varphi_7 \) and \( \varphi_8 \) torsion angles and suggest the only favorable positions of the alkyl substituents (Table 1S – Supplementary information).

We have found that the conformation of the LC4 chiral component affects its dipole polarization and, thus, the dipole polarization of the whole cell. Obviously, the conformation of the chiral component LC4 affects the spatial packing of molecules in the liquid-crystal phase, which can also affect the dipole polarization of the phase. Therefore, in the next step the analysis of the set of possible minimum cell packing was performed in order to find the laying of low- and high-polarized phases. We assumed that each packing of minimal cell corresponds to a certain conformer of the LC4 chiral component, so that the search for possible packing was simultaneously a determination of the set of LC4 conformers realized in the liquid crystal phase.

Calculation of bias exchange well-tempered metadynamics for the minimal cell with previously determined mutual orientations of the components of the liquid-crystal phase enable
us to express the dependencies of the free energy, $\Delta G_\phi$, on the torsion angles $\phi_1$-$\phi_8$, which determine the variety of possible LC4 chiral component conformers and are presented in Fig. 4.

The transformation of one packing into another implies a change in the conformation of the LC4 chiral component. The heights of the energy barriers separating the different packing of the minimum cell are estimated (Table S2 – Supplementary information) from the free energy profiles, depending on the corresponding torsion angles (Fig. S4– Supplementary information). The minimal free energy of the minimal cell, $\Delta G_{\text{cell}}$, varies for the revealed packing of the minimal cell in the range from -68 to -19 kJ/mol. The most energy favorable packing ($\Delta G_{\text{cell}}$ = -68 kJ/mol) contains the LC4 conformer, characterized by the transoid conformation of the carbonyl groups and the smallest dipole polarization (Table S3– Supplementary information). This is the packing that has been chosen to construct LPP, and the conformer contained in it is called as LPCC. The packing that is the third in terms of energy gain ($\Delta G_{\text{cell}}$ = -65 kJ/mol) also contains the LC4 conformer with the transoid conformation of the carbonyl groups. It differs from LPCC by the conformation of the sec-hexyl substituent in the ester group, which corresponds to a change in the $\phi_5$ torsion angle (Fig. 4). We have found that such a difference in the conformation leads to an increase in the minimal cell polarization relative to LPCC chosen for constructing LPP. This is illustrated by Fig. 7, which shows that all the components of the polarization vector $\mathbf{P}$ and its projection onto the $yOz$ plane $\mathbf{P}_{yz}$ increase in HPP relative to LPP. The polarization of the LC4 chiral component also increases. The transition of the LPP minimal cell to the third minimal cell in terms of $\Delta G_{\text{cell}}$ implies the $\Delta G_{\phi_5}^{1\rightarrow 2}$ energy barrier of 13 kJ/mol. Thus, the third minimal cell in order of energy has a sufficiently favorable $\Delta G_{\text{cell}}$ and exceeds LPP in polarization. Also this minimal cell is derived from LPP by alteration of one torsion angle of the LC4 chiral component. This alteration is accompanied by the corresponding rearrangement of the minimal cell, implying the transition over a sufficiently low energy barrier. These facts enable us to select this minimal cell for construction of HPP, and set the LC4 conformer contained in it to HPCC.

<table>
<thead>
<tr>
<th>Minimal cell</th>
<th>$\phi_1$</th>
<th>$\phi_2$</th>
<th>$\phi_3$</th>
<th>$\phi_4$</th>
<th>$\phi_5$</th>
<th>$\phi_6$</th>
<th>$\phi_7$</th>
<th>$\phi_8$</th>
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<td>83°</td>
<td>74°</td>
<td>-3°</td>
<td>-3°</td>
</tr>
<tr>
<td>High-polarized state</td>
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<td>169°</td>
<td>-177°</td>
<td>147°</td>
<td>147°</td>
<td>83°</td>
<td>13°</td>
<td>1°</td>
</tr>
</tbody>
</table>
Table 1. Torsion angles of the LC4 chiral component in the LPP and HPP minimal cells

The packing of components in the minimal cells of LPP and HPP (Fig. 6b), has its similarities and differences. At first, let us focus on their similarity that is mainly manifested in the terphenyl and phenylpyrimidine fragments laying. The terphenyl fragment of the LC4 chiral component forms the π-stacking interaction with phenylpyrimidine fragments of LC1(a) on one side and with LC2(a) on the other (Fig. 6b). This “triple stack” is expanded in the Oy direction by additional interactions with the LC3(a), LC3(b), and LC2(b) molecules stacked in the “triple bundle”. In this case, LC2(b) forms orthogonal contact with LC1(a), and both the phenylpyrimidine fragments of LC3(b) and LC2(a) lie in the same plane. On the other side of “triple stack”, the phenylpyrimidine fragment of LC1(b) is coplanar to the same LC2(b) fragment of abovementioned “triple bundle”. Thus, the packing of molecules in the minimal cells of LPP and HPP is almost the same, but it slightly differs by the conformations of alkyl chains in LC1, LC2, LC3, as well as by the conformation of one of the sec-hexyl substituents in LC4.

Now let us pay attention to the packing differences in the minimal cells of LPP and HPP. They differ in locations of the LC1(c) and LC3(c) molecules on the other side of the “triple stack”. In the LPP minimal cell, the LC1(c) molecule is located so that in the liquid-crystal phase its phenylpyrimidine fragment forms π-stacking interaction with the same fragment of LC3(a) of the “triple bundle” of the neighboring minimal cell. Aromatic cycles of LC3(c) and the same fragments of LC1(c) and LC3(a) of the neighboring minimal cells form the orthogonal orientation. In contrast, in the HPP minimal cell, the LC1(c) molecule shifts along Ox and rotates in such a way that it almost completely loses π-stacking interaction with the phenylpyrimidine fragment of LC3(a) of the “triple bundle” of the neighboring minimal cell. The LC3(c) molecule shifts along Ox and rotates in such a way that it forms the orthogonal contact with the phenylpyrimidine fragment of LC1(c) of the same minimal cell, losing the orthogonal contact with the phenylpyrimidine fragment of LC1(c) of the neighboring minimal cell. In HPP, the LC1(c) and LC3(c) molecules shift inversely to the Ox axis in one direction relative to the “triple stack”.
The polarization, $\mathbf{P}$, of HPP predictably exceeds that of LPP (Fig 7). The main contribution to its superiority is made by the greater dipole polarization of the LC4 chiral component, which predominates in the $P_z$ vector component.

The $P_x$ vector component of the LC2 and LC3 achiral components dipole polarizations is also redistributed into $P_z$ upon LPP to HPP transition, whereas the $P_y$ and $P_z$ vector components of the LC1 dipole polarization are redistributed into the $P_x$ vector component (Fig. S2 – Supplementary information).

Figure 6. a) the simulated LPP fragment. b) Superimposition of LPP (semitransparent sticks) and HPP (nontransparent sticks) minimal cells.

One can be assumed that this redistribution is associated with the differences in packing of the LC1(c) and LC3(c) molecules described above. Changes in the sec-hexyl substituent conformation of the LC4 chiral component are able to directly affect only the conformations of alkyl substituents of other components of the liquid-crystal phase. However, the increase in the $P_z$ vector component of the LC4 chiral component dipole polarization caused by these changes is able to provoke packing rearrangement of the LC1(c) and LC3(c) molecules, disrupting the mutual compensation of the dipole polarizations of the LC1 and LC3 molecules, which mainly affects the $P_z$ vector component (Fig. S3 – Supplementary information). The polarization that occurs in HPP makes a significant contribution to the increase in the phase polarization,
comparable with the contribution introduced by the increase in the LC4 chiral component polarization.

Figure 7. Polarization of the low-polarized (LPP) and high-polarized (HPP) phases: a) the magnitudes of the polarization vector projections on the yOz plane for each phase component; b) phase polarization

The calculation of the orientation entropy and the nematic order parameter shows that HPP is slightly more ordered ($S=0.80\pm0.02$) than LPP ($S=0.70\pm0.02$), because of the ordering effect of the much greater dipole polarization of the LC4 chiral component. LC1 and LC4 are more highly ordered in HPP than in LPP, and, conversely, LC2 and LC3 are more ordered in LPP (Fig. 8a).
Figure 8. a) Orientation entropy of low-polarized (LPP) and high-polarized (HPP) phases; b) The angle $\alpha$ of the deviation of the long axes of the molecules from the Ox axis for the low-polarized (LPP) and high-polarized (HPP) phases.

With that, HPP is characterized by smaller deviation $\alpha$ of the long axes of all molecules from the Ox axis than LPP (Fig. 8b). The estimation of the permittivity $\varepsilon$ has yielded the values of 1.8$\pm$0.1 for LPP and 1.9$\pm$0.2 for HPP.

4.2. Comparison of simulated and experimental results

The simulated material parameters (spontaneous polarization and high frequency permittivity) of the CHS1 mixture are in good accordance with experimentally measured ones (sections 2.3 and 2.4). As follows from Fig. 7, the spontaneous polarization of LPP (54 nC/cm$^2$) is very close to the experimentally measured value $P_s=42$ nC/cm$^2$ (room temperature). Contrarily, the MD simulated value of spontaneous polarization of HPP (148 nC/cm$^2$) is far from the experimental one. However, both the high frequency permittivities ($f\rightarrow\infty$) of LPP ($\varepsilon=1.8\pm0.1$) and HPP ($\varepsilon=1.9\pm0.1$) are very close to its experimental value ($\varepsilon\approx1.98$). This result could be explained by the dominant contribution of the electronic polarization rather than conformational effects.

As consequence of above described comparison, one can conclude the constituting molecules of multicomponent FLC mixture components of the mixture are arranged in such way to form the low polarization state. Moreover, the knowledge of the experimental values of the spontaneous polarization allows to predict the conformational state of the chiral component.

Conclusion

In summary, the method of metadynamics in the version of bias exchange well-tempered metadynamics was used to model the properties of the multicomponent ferroelectric liquid crystal mixture. The structure of the simulated FLC was investigated in the set of phase states that arise when the conformation of the chiral component was varied during the metadynamics simulation. The revealed structures of low- and high-polarized SmC* phases in general have similar packing of the phenylpyrimidine and terphenyl fragments, differing both in the conformation of the LC4 alkyl substituent and in the packing of the LC1(c) and LC3(c)
molecules. The materials parameters of the modeled low-polarized FLC configuration is in good agreement with experimentally measured material characteristics of CHS1 (the dielectric permittivity $\varepsilon$, tilt angle and the spontaneous polarization). The higher values of polarization of high-polarized configuration compared to low-polarized one could be explained by both an increase in the polarization of the LC4 chiral component and a violation of the mutual compensation of the dipole moments of the achiral components.

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Highlights

- Spontaneous polarization of multicomponent FLC mixture depends on the conformation state of the chiral component
- Structural properties of FLC mixture depend on the conformation state of the chiral component
- MD simulation and electrooptic measurements can be used to identify the conformation state of the chiral component