Chiralization and ferroelectric state induction in nanostructured liquid crystals

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Abstract. The liquid crystals (LC), due to their naturally high bulk ordering, strong birefringence and easy electrooptical driving, serve as matrix in the nanocomposites doped with non-mesogenic or mesogenic nanoparticles. The nanocomposite’s structural units exhibit very complex molecular form indicating the strength and the intermolecular interaction between the matrix and dopant’s molecules. Hydrogen bonds are of particular significance for the formation of the nanocomposite structural units, since the symmetry of the LC nanocomposite could be controlled and controllably decreased due to the acceptor–donor interaction between the dimeric matrix and the dopants. As a result, the LC nanocomposite can reach the lowest symmetry, known as triclinic - C1. Using the LC p,n-alkyloxybensoic acids (nOBA) in form of hydrogen-bonded dimers as matrix and non -mesogenic - single wall s carbon nanotubes (SWCNT), perfluorooctanoic acid (PFOA), 4-hydroxypiridin (HOPY) or mesogen - cholesteryl benzoate (ChB) as dopants and choosing optimal concentrations (where the typical LC state was preserved), we obtained nanocomposites 7OBA/SWCNT, 7OBA/PFOA, 9OBA/HOPY and 8OBA/ChB. We indicate two forms of ferroelectricity in the studied nanocomposites: developable ferroelectricity, characteristic for the 9OBA/HOPY, 7OBA/PFOA compounds and developed ferroelectricity characteristic for 8OBA/SWCNT, 8OBA/ChB.

1. Introduction

It is possible to control the optical and electro-optical properties of the liquid crystals (LC) by changing the molecular arrangement, inserting external agents (organic, in particular mesogenic, and nonorganic), usually specially functionalized nanoparticles with different structures sizes and shapes [1-5]. Since, the liquid crystalline state combines order and mobility at the molecular (nanoscale) level, molecular modification can control nano-scale assembly and the way how surface-treated nanoparticles can interact with liquid crystals, so that the macroscopic properties of the LC host can conform to specific applications.

Mixtures of liquid crystals with nonmesogenic materials (wide range of nanosize rodlike particles, such as carbon nanotubes, metallic or semiconducting nano-spheres and wires) are promising materials for the contemporary nanocomposites, able to create a new trend in the LC photonic techniques [6-18]. New family of nanoparticles, like single walled carbon nanotubes (SWCNT), CdSe quantum dots [19], hydroxypridine [20] and perfluorooctanoic acid (PFOA) [21] or mesogen, like cholesterol benzoate ChB [22] has recently been introduced, exhibiting a great capability for homogeneous dispersions in liquid-crystal matrix and ability to alter its inherent bulk properties.
The classical p-n-alkyloxybenzoic acids (nOBA) LC are the basic components in forming supramolecular systems [23]. On the other hand, otherwise achiral nOBA LC, as an effect of the dimeric structure conformation, makes it possible to create an induced chirality [24].

In the present work we prepare mixtures of some homologues of achiral p-n-alkyloxybenzoic acids with homologues numbers 7,8,9 (7OBA,8OBA,9OBA) with non-mesogenic nanoparticle SWCNT in different concentrations. In our previous investigations [24] we found that in most of these concentrations, new chiral phases were produced and depending on the cell thickness and the anchoring energy magnitude, the new unique smectic G phase may or may not be induced. Furthermore, setting out for creating an adequate molecular and macroscopic model of smectic CG phase, we are going to unify the interactions between 7,8,9OBA with mesogens, like cholesterol benzoate (ChB) or non-mesogens like SWCNT, 4-hydroxypiridine (HOPY) and perfluorooctanoic acid (PFOA) regarding the compatibility and thermal stability of the nanocomposites.

2. Experimental results and discussion

The experiments have been carried out on a nanocomposites of the LC 4, n-alkyloxybenzoic acids with n=7,8,9 (7,8,9OBA) supplied by Sigma-Aldrich (Product of Japan), with non-mesogens: i) single walled carbon nanotubes (80BA/SWCNT) ii) 4-hydroxypiridin (HOPY) - 7OBA/HOPY, iii) perfluorooctanoic acid (PFOA) - 7OBA/PFOA, as well as with mesogen material – iv) cholesteryl benzoate (ChB) - 8OBA/ChB.

Let us note that for the nanocomposites we choose the optimal combinations and corresponding concentrations of LC matrix (homologues of nOBA) and mesogen or non-mesogen components, for the novel achiral, chiral, or ferroelectric phases to be induced. The attention to non-ferroelectric smectic G or ferroelectric smectic CG phases will be heightened. Thus unifying the problem, we emphasize mainly on the micropolarization, electrooptical and comparative textural analysis.

2.1. The nanocomposite 7OBA/SWCNT

The general molecular structure of the nOBA molecule is given below.

In the bulk of the nanocomposites the basic structure unit – dimer ring - may reduce its local symmetry and transform into open dimer by breaking one of the linear H-bonds. The open dimers can further undergo bending at the unbroken H-bond, thus adopting a shape similar to the bent-core banana molecules [25,26]. In this way, it creates the characteristic parameters – polar vector $\mathbf{P}$ and a vector perpendicular to the plane of the bent dimer $\mathbf{m} = \mathbf{n}_1 \times \mathbf{n}_2$, where $\mathbf{n}_1$ and $\mathbf{n}_2$ are unit vectors pointing along the two wings of the dimer. $\mathbf{m}$ is the so called kink vector and its magnitude represents the degree of bending of the dimer. As a result, this produces the premise for the lowest possible symmetry triclinic $C_1$ of the nanocomposite structure.

A variety of phases are observed at SWCNT concentration of 0.01 weight % in LC cell with thickness $d = 8\mu m$. After briefly crossing the conventional N phase in an interval of $\approx 1^\circ C$, the nanocomposite forms a chiral nematic phase (N*) at 142°C. Then the system enters at 93°C into a chiral smectic C (Sc*) phase (on figure 1(a) the transition N* $\rightarrow$ Sc* is depicted). The textures of N* and Sc* are characterized by typical stripes indicating the helix direction, which in this case lies in the xy cell plane or is tilted with respect to it. Upon further cooling, at 90°C a reentrant chiral nematic (Nr*) phase is reached. Figure 1(b) presents the Nr* texture. At 86°C we observe a transition from Nr* to a low-temperature smectic phase (figure 1(c)), which is fluid (well indicated by small colored glass particles), not smooth, and colored in red and green mosaic domains, thus closely resembling the CG phase. At very slow cooling ($0.1^\circ C \text{ min}^{-1}$) starting from the I phase, the domains grow as fractal nuclei and coalesce into large areas with opposite optical rotation (distinct circular dichroism). Investigating
this low-temperature smectic phase we observe that upon sample rotation in either direction, the red color turns into green and vice versa. Besides this variable birefringence (red and green colors), on entering this phase from the N∗ one we also observe a change in fluidity and the texture loses its smoothness appearing as a colored mosaic texture with equal left- and right-handed helices. This unambiguously shows that this phase is chiral and biaxial. The properties of this phase imply a drastic symmetry breaking of the constituent LC molecules. Differently from the conventional S_C phase of pristine 7OBA where the open dimers can only undergo twisting, the observed combination of chirality and biaxiality implies a loss of the linear shape of the LC molecules, i.e., formation of a bent-dimer shape.

Figure 1. 7OBA/SWCNT textures (c=0.01wt%) in a nonoriented LC cell with thickness d=8 μm: (a) Phase transition from N∗ to S_C at T=93°C; (b) Reentrant N∗ phase at T=89°C; (c) Low-temperature smectic C_G phase at T=86°C.

Reducing the cell thickness to 8 μm increases the anchoring energy and imposing unidirectional surface alignment lowers the symmetry similarly to the case when an external pressure is applied to the system. The reentrant nematics indicates that at these surface and temperature conditions monomers and open dimers dominate in the LC system and suppress the smectic layering, thus leading to a return of the long-range positional order typical for N phases. At further cooling, however, the bent dimers gain dominance and restoration of the smectic layering then leads to a fluid tilted smectic C_G state (without positional order inside the layers).

The most important problem is the compatibility of the conformed LC dimers and the SWCNT. To check the results from the microtexture analysis we performed a comparative monitoring of the different Raman spectra of 7OBA/SWCNT in parallel polarization at several temperatures (quoted in the plot) in the low-frequency region (100–1300 cm⁻¹) (figure 2). The lowest three traces are spectra of pristine 7OBA for comparison. The peak at 310 cm⁻¹ appearing in the S_C phase is marked by arrows and the symbol SC. The sharp peaks emerging upon transition to the Cr state are marked with asterisks. The inset shows at an expanded scale the RBM region of the 7OBA/SWCNT spectrum at 82°C and a spectrum of pristine SWCNT heated to 82°C before mixing to the LC.

With the radial breathing mode (RBM) centered at about 177 cm⁻¹ the signature of carbon nanotubes is clearly visible in the spectra of 7OBA/SWCNT, confirming the presence of small SWCNT bundles in the nanocomposite. Except for the RBM no essential differences between 7OBA/SWCNT and pure 7OBA are found in their Raman spectra from the I phase down to 100°C, but upon further cooling a number of significant changes occur. Along with the N → S_C transition in pure 7OBA, a specific peak appears at 310 cm⁻¹ as evident from the spectrum at 94°C (see figure 2). This peak can serve as a distinguishing feature of the S_C phase in 7OBA as it represents the only difference in the Raman spectra of this substance between the N and the S_C phase. The transition to a solid phase causes remarkable further changes, as can be seen from the lowest spectrum on figure 2 taken at 82°C: Additional peaks appear at 150, 178, 252, 351, 885, and 1148 cm⁻¹; the bands at 105 and 638 cm⁻¹ split into two and that at 777 cm⁻¹ into three sharp peaks.
Figure 2. Raman spectra of 7OBA/SWCNT and pure 7OBA in parallel polarization at several temperatures (quoted in the plot) in the low-frequency region (100–1300 cm\(^{-1}\)).

We now analyze the Raman spectra of the 7OBA/SWCNT nanocomposite starting with the \(N^\ast\rightarrow S\_C^\ast\) transition expected at 94°C. The corresponding spectrum for 94°C in figure 2 indeed contains the peak at \(\approx 310\) cm\(^{-1}\) identifying the smectic phase although this peak is slightly softened and broader compared to that of pure 7OBA. In the next spectrum taken at 91°C this peak is absent which is consistent with the reentrant nematic phase from 93°C to 88°C established by the microtexture analysis. The spectrum taken at 82°C contains again a sharp and relatively intense peak at 310 cm\(^{-1}\) and resembles in its structure the pure 7OBA spectrum at 94°C thus indicating a smectic phase. Hence the behavior of the \(C\_G\) phase in Raman scattering is similar to that of the conventional \(S\_C\) phase. Finally, the spectrum taken at 71°C closely resembles the pure 7OBA spectrum at 82°C with all additional sharp peaks indicating solidification of the nanocomposite. The Raman spectra of 7OBA/SWCNT are thus consistent with the sequence of phase transitions found by microtexture analysis in this nanocomposite. The richer phase development in 7OBA/SWCNT is undoubtedly connected to an interaction of the LC molecules with the nanotubes and it would be interesting to find evidence for this interaction in the Raman spectra. Such interaction should stem from the intermolecular overlap of \(\pi\) orbitals (\(\pi\) stacking). The RBM band with vibrational pattern perpendicular to the nanotube-bundle axis can serve as a sensitive probe for interactions of SWCNT with molecules in contact with their surface, as well as for interactions among the SWCNT themselves, e.g., within a bundle [24]. As the 7OBA molecule also contains phenyl rings, it is logical to expect its interaction with the SWCNT to be reflected in the behavior of the RBM band of 7OBA/SWCNT. Comparing Raman spectra of the pristine SWCNT powder before mixing it into the liquid crystal with spectra of the 7OBA/SWCNT nanocomposite, we find indeed a slight RBM hardening and redistribution of its intensity in the 7OBA/SWCNT spectra. This comparison is depicted for the \(C\_G\) phase in the inset of figure 2 for \(T = 82°C\). The RBM band of the SWCNT used in the present study consists of three features: a main peak and two shoulders on both sides. For the pristine tubes their frequencies were determined as follows: 159.5, 176, and 188 cm\(^{-1}\). In the 7OBA/SWCNT spectra the low-energy shoulder hardens by 3 cm\(^{-1}\), the main RBM peak by 1 cm\(^{-1}\), and the high-energy shoulder also by 1 cm\(^{-1}\) with simultaneous transfer of spectral weight from the low-energy to the high-energy shoulder. We consider this clear evidence for interaction of the LC molecules with the nanotubes and regard this interaction as the factor breaking the one H bond in the
central hexagon and leading to a bent-dimer shape of the 7OBA molecules in the nanocomposite, which is the main condition for nanoscale symmetry reduction to C₁ and C₆ state growth. The main feature of this phase is the out-of-layer-plane electric polarization (induced upon dimer bending), which is bulk, permanent and unlike the popular ferroelectric Sc* closely resembles solid state ferroelectrics. The detection and evaluation of such out-of-layer-plane polarization is delicate and can be done by corresponding electro-optical excitations.

It is known that the patterns formed at phase transition LC → isotropic (I) phase require \( \text{div } P = 0 \) [27]. As already mentioned, C₆ develops out of smectic layer plane’s polarization (\( P_{\text{out}} \)), unlike Sc* where the polarization is situated in parallel to the plane of the smectic layers and directly satisfies \( \text{div } P = 0 \). To satisfy the requirement \( \text{div } P_{\text{out}} = 0 \) in C₆ state, however, a compensation of the divergence of the out-of-smectic layer polarization, is needed. So in the presence of 10 Hz ac electric field the chiral structures (usually with ribbon or ropelike forms) shrink in correlation with the polarity inversion and cause additional elastic-deformation for compensation of the free energy of the LC system, thus ensuring the \( \text{div } P_{\text{out}} = 0 \) to be satisfied. When \( E \) is opposite to \( P_{\text{out}} \) the free energy increases by \( P_{\text{out}} · E \) inducing a transition from C₆ to above-lying phases up to the I state. Especially, for an electric field of at least 1.6 \( \text{V/μm} \), we observed such a transition between developed chiral states C₆ and Sc*⁰. We thus have electric-field induced phase transition governed by temperature-dependent threshold field. In other words, we observe an equivalent decrease of the phase transition temperature driven by the electric field [28].

Using the ferroelectrically induced decrease \( \Delta T \) of the phase transition temperature, we can assess the polarization by the modified Kirkwood-Helfrich equation [27-29]: \( \Delta T/\Delta H/Mρ = 0.5ε_a ε_o |E|^2 - |P||E| \cos α \), where \( T_o \) is the C₆ → Sc*⁰ → I transition temperature at \( E = 0 \), M is the molar mass, \( ρ \) the density of the nanocomposite, and \( α \) is the angle between \( P \) and \( E \). Thus we estimate that \( P_{\text{out}} \approx 110 \text{nC/cm}^2 \). Such a low-temperature smectic state we define as developed C₆.

2.2. The non-mesogen nanocomposite 7OBA/PFOA
The perfluorooctanoic acid (PFOA) was supplied by Sigma - Aldirch (product of China). The intermolecular hydrogen-bonded nanocomposites are synthesised by mixing 7OBA and PFOA in 1:1 ratio in ethanol. The molecular structure of the nanocomposite 7OBA/PFOA is presented as follows:

In this nanocomposite, twisted X-shaped elementary chiral units (shown in figure 3(a)) emerge 2.5°C below the isotropic phase. The left and right chiral senses are well seen (e.g., (1) and (2) in figure 3(b)). On further cooling, these chiral centers coalesce. This second stage of the chiral structure development provides large chiral monodomains indicating formation of spontaneous twofold chirality (figure 3(c)). The second twist stage yields the macroscopic effect, involving a strong texture change: left- and right-handed chiral domains grouped in regions partially separated by \( 2\pi \) walls (see figure 3(c)). However, here the C₆ state is confined only in the domains and does not spread in the whole nanocomposite. This kind of C₆ state will be referred to as developable state. The developable chiral structure is very well pronounced in this case. One notes chiral ribbons (HRs) of both helicities, indicating the presence of left and right molecular or structural twists.

To analyze the properties of the nanocomposite 7OBA/PFOA and also to detect the polarization, \( P \) we performed electro-optical measurements. Applying low-frequency electric field (less than 50Hz) applied across a 12µm thick LC cell, one observes the appearance of well-pronounced chiral ribbons (HR) (see figure 4(a)).

The HR coalesce into wide chiral ribbons upon increasing the field magnitude (figure 4(b)). We chose sufficiently low frequency for the polarization to be able to follow the polarity inversion. The ribbons twist into right- or left-handed spirals depending on the polarity. To compensate this twisting,
an additional deformation (coiling up) of the rope- and ribbon-like texture domains arises. Following
the polarity of the external field, the spirals are formed clockwise or counterclockwise. This effect
indicates that the ribbons are polar and the polarization vector \( \mathbf{P} \) has a component parallel to the
substrate surface. Coiling of chiral structures is another compensatory mechanism to make the
polarization satisfy \( \text{div} \mathbf{P}_{\text{out}} = 0 \).

**Figure 3.** Microtextures of 7OBA/PFOA in LC cells with glass substrates and \( d=12\mu\text{m} \): (a) The emergence of the twisted X-shaped elementary chiral units at \( T=118^\circ\text{C} \); (b) Left-handed (1) and right-handed (2) chiral units at \( T=117^\circ\text{C} \); (c) Large chiral monodomains with twofold spontaneous chirality formation at \( T=104^\circ\text{C} \).

**Figure 4.** Electrically induced chiral ribbons (indicated by arrows) of 7OBA/PFOA in LC cell with ITO/glass substrates and \( d=12\mu\text{m} \): (a) \( E=1.7\text{V/\mu m} \); (b) \( E=7.5\text{V/\mu m} \). Frequency 50Hz. \( T=111^\circ\text{C} \).

The appearance of the \( 2\pi \) walls in the presence of electric field and the absence of \( \pi \)-walls
(characteristic for non-chiral state) indicates a presence of residual polarization [30-32]. The formation
of \( 2\pi \) walls is an imprint of the spontaneous polarization, i.e., the polar symmetry of the director,
unlike the \( \pi \) walls indicating quadrupolar symmetry as that of achiral Sc phase. As was indicated in
[33], the nature of the polar response and the symmetry of the \( \mathbf{P} \)-director can be determined from the
director’s inversion walls, since the texture reflects the response to applied electric fields by
reorientation of the director.

The magnitude of the polarization can be estimated from the wall width upon application of an in-
plane electric field \( E \) [33]. The \( 180^\circ \) rotation of the director following each field reversal results in the
formation of \( 2\pi \) walls. The ferroelectric term \( f_p = -\text{P.E} \) exhibits coupling to the spontaneous
polarization $\mathbf{P}$. These contributions result in a correlation length $\xi_p = \frac{\sqrt{EP_s}}{K}$ where $K$ is the mean Frank elastic constant in a one-constant approximation [29]. The inversion wall width $w$ clearly scales as $1/E^{1/2}$ (figure 5).

![Figure 5. The $2\pi$ wall width dependence on the electric field.](image)

From the slope of the fit, we estimated a spontaneous polarization with a magnitude of about 0.25nC/cm$^2$.

The developable $C_G$ state could be indicated also by Raman spectral analysis. In figure 6 we show temperature-dependent Raman spectra of the nanocomposite 7OBA/PFOA.

![Figure 6. Raman spectra of the 7OBA/PFOA nanocomposite at different temperatures.](image)

Between 145 and 99$^\circ$C the nanocomposite 7OBA/PFOA displays the Raman signature of a nematic phase: the peak at 310 cm$^{-1}$, characteristic of the smectic phase, is smeared out, very faint or missing;
there is a weak single peak at 635 cm\(^{-1}\) and the doublet at 836 cm\(^{-1}\) and the lines at 1130, 1170 and 1254 cm\(^{-1}\) have relatively low intensity. Slightly above 92°C the system undergoes a transition to solid crystal state manifested by a pronounced sharpening of all spectral lines and appearance of numerous new sharp lines at 147, 176, 248, 307, 348, 400, 760, 775, 792, 882, 1009 and 1146 cm\(^{-1}\). Additionally, the peak at 635 cm\(^{-1}\) transforms into a sharp doublet at 640 cm\(^{-1}\) and the doublet at 836 cm\(^{-1}\) undergoes a significant intensity redistribution and sharpening. Interestingly, a distinct smectic phase could not be detected with Raman spectroscopy and micropolarization analysis but at 99°C already some precursors of the additional sharp lines (e. g. of the triplet at 760 - 792 cm\(^{-1}\)) are observed. This implies that a gradual transition from the nematic state directly into the solid crystal state may be taking place and the developable smectic state can be recognized by subtle changes in the spectra between 100°C and 92°C.

The other nonmesogen dopant HOPY, similarly to the PFOA also display developable C\(_G\) state.

2.3. The non-mesogen nanocomposite 9OBA/HOPY

In a nanocomposite 9OBA/HOPY the liquid crystal matrix of 9OBA operates as a N-bonding donor and HOPY serves as a H-bonding acceptor. The building blocks of the induced 9OBA/HOPY nanocomposite could be schematically presented as is shown below

\[
\begin{align*}
\text{R} & \quad \text{O-H-N-} \\
\text{O} & \quad \text{OH}
\end{align*}
\]

Staring with slow cooling (0.1°C/min) from the isotropic phase we obtained consecutively the well formed developable chiral textures - helical chiral ribbons (figure 7), spiral cords (manifesting the nucleation and development of the chiralization) and surrounding green and red (orange) left and right handed domains, reflecting the developed chiral domains and strongly resembling the features of the C\(_G\) phase.

**Figure 7.** 9OBA/HOPY texture of well formed developable chiral and helical chiral ribbons in LC cell with glass substrates and d=12μm. T=135°C.

Applying the same procedure of the electrical field action using \(dc\) or low-frequency \(ac\) voltages, as that presented in the case of the nanocomposite 7OBA/PFOA, we estimated the polarization value in the developing chiral range to be 0.15 nC/cm\(^2\).

Differently from the nonmesogens PFOA and HOPY and similarly to SWCNT, nanocomposites with the mesogenic dopant cholesteryl benzoate (ChB) display developed C\(_G\) state.

2.4. The mesogen nanocomposite 8OBA/ChB

In such nanocomposite a parallel molecular dipole orientation (a significant dipole moment \(\mu \approx 2.4\)D (Debye) perpendicular to the long molecular axis) of the dissolved chiral molecules is created. A result of this parallel orientation is the appearance of spontaneous polarization \(P\) and eventually ferroelectric state induction. The nanocomposite structural unit is indicated below:
At slow (0.1°C/min) cooling from the isotropic phase we go to formation of chiral nematic N* phase (figure 8(a)).

Applying 20V dc or 20V, 20 Hz ac electric fields one observes appearance of $2\pi$ walls (figure 8(b)). Its width linearly decreases as $E^{-1/2}$, allowing the polarization of the developable chiral structure to be evaluated (less than 0.1nC/cm²). Below 114°C a chiral mosaic phase grows (figure 8(c)), considerably resembling in textual respect the developed smectic C G state. The small values of the polarization, within the developable range, where the $2\pi$ wall exist, do not allow evaluation of the polarization value in the developed chiral state in figure 8(c).

3. Conclusion

The general result is: each of the studied nanocomposites is constituted of structural units with various complex shapes, determined by the strength and specificity of the interaction between the dopant structural units and the dimer rings. This interaction combined with the surface anchoring, bulk and electrical actions, leads to drastic reduction of the LC system symmetry. As a result, transition from achiral state, characteristic for the pristine nOBA substances in the N and Sc states (with D∞h and C2v symmetry), to chiral low-symmetric states, including ferroelectric smectic C* with C2 symmetry and ferroelectric smectic C G with the lowest C1 triclinic one takes place. We identify the chiral nucleus generation, and the growing ribbon-like and helical structures, as developable smectic C G states. Their response to temperature decrease or to application of dc and low-frequency ac electric fields shows the presence of a residual (spontaneous) polarization.

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