Liquid crystal nanocomposites produced by mixtures of hydrogen bonded achiral liquid crystals and functionalized carbon nanotubes

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Abstract. The liquid crystalline (LC) nature of alkyloxybenzoic acids is preserved after adding of any mesogenic or non-mesogenic compound through hydrogen bonding. However, this non-covalent interaction provokes a sizable effect on the physical properties as, e.g. melting point and mesomorphic states. In the present work we investigate nanocomposites, prepared by mixture of the eighth homologue of p-n-alkyloxybenzoic acids (8OBA) with single-walled carbon nanotubes (SWCNT) with the purpose to modify the optical properties of the liquid crystal. We exercise optical control on the LC system by inserting SWCNT specially functionalized by carboxylic groups. Since the liquid crystalline state combines order and mobility at the molecular (nanoscale) level, molecular modification can lead to different macroscopical nanocomposite symmetry. The thermal properties of the functionalized nanocomposite are confirmed by DSC analyses. The mechanism of the interaction between surface-treated nanoparticles (functionalized nanotubes) and the liquid crystal 8OBA bent-dimer molecules is briefly discussed.

1. Introduction
The nanostructured liquid crystals (LC) are of academic and industrial interest as they exhibit in many instances significantly different properties from those of distinct atoms or bulk materials [1-5]. It is possible to control the optical properties of liquid crystals by changing the molecular arrangement, inserting external agents, e.g., various non-mesogenic nanoparticles. The concentration of the nonmesogenic component, its homogeneity and its compatibility with the liquid crystal is of particular significance for the structural, optical and electrical properties of the nanocomposite. This effect is expected to be more controllable when the inserted external nanoparticles are specially functionalized. The high value of the surface-bulk ratio makes the physical properties of nanoparticles rather unique. Single-walled carbon nanotubes (SWCNT) are a special category of such nanoparticles which additionally offer a highly anisotropic impact on the LC due to their large aspect ratio [6-9]. They also exhibit a great capability for homogeneous dispersion in a liquid-crystal matrix and ability to alter its inherent bulk properties [6]. The coupling of the anisotropic elasticity of the LC medium to the optical, conductive, or magnetic properties of functionalized nanoparticles is expected to have a significant
impact on the macroscopic properties of LCs designed for contemporary nanotechnology. Since the LC state combines order and mobility at the nanoscale level, even small quantities of SWCNT can effectively control the LC nanoscale assembly, which provides specific material properties.

The classical p-n-alkyloxybenzoic acid (nOBA) LC is the basic component in forming supramolecular systems. Even without complementary nonmesogenic molecules it displays a supramolecular state due to the dimeric form of its molecule, and its donor ability at contact with a nonmesogen substance predicts rich mesomorphic states [10]. On the other hand, its dimeric structure allows an induced chirality although it is an achiral LC system, i.e. it is a hopeful candidate for the realization of the long sought-after C₁ symmetry in LC systems like the bent-core molecules [11].

Recently [12,13], we investigated a series of nanocomposites, built of the hydrogen-bonded liquid crystal 7OBA and SWCNT by optical microtexture analysis and other complementary methods. The bulk interactions of the dimeric LC molecules with the SWCNT turn out to mainly govern the type (symmetry), thermal stability and chirality of the LC states induced in these nanocomposites. As a result, a cascade of phase transitions and phases not typical for pristine 7OBA are observed. The most intriguing result is the detection of a triclinic smectic C\textsubscript{G} phase, which is chiral and biaxial, and exhibits bulk ferroelectricity. To explain this phenomenon, we assumed that the SWCNT embedded in the liquid crystal matrix, could also affect the structure of the constituent LC molecules. This is particularly important when these molecules are dimers and especially, dimers formed by linear hydrogen bonding (H-bonding) since the non-mesogenic component in the nanocomposite could provoke a conformation of the LC molecule from a closed dimer to a opened dimer (bent-dimer) or even monomer, which may lead to new electrical and thermal properties, including new phases. Recently, a smectic G phase was induced through intermolecular hydrogen bonding between mesogenic p-n-alkyloxybenzoic acids and nonmesogenic p-aminobenzonitrile [14], due to the H-bonding between the electron-rich terminal cyano group (as proton acceptor) and the terminal carbon of the COOH group of nOBA. This smectic G phase, however, was not interpreted as the sought-after smectic C\textsubscript{G} phase.

The closed dimers can also be viewed as flexible bent-core-like molecules, showing similarities with phases found in large-size banana-like system [11], but exhibiting a more complex structure. A close similarity was suggested between the smectic X phase found in these substances and the C\textsubscript{G} phase or its analogue B\textsubscript{7} phase in the bent-core LC [11]. These phases are examples of the typical smectic states where left- and right-handed helices are induced in an LC system whose constituent molecules are achiral. The smectic C\textsubscript{G} phase was predicted long ago by de Gennes [15]. Being biaxial and fluid in the layers and having a macroscopic handedness due to its structure, this phase is a natural candidate to demonstrate induced helices in a system composed of achiral molecules.

In the present work we examine nanocomposites of the eighth homologue of non-chiral p-n-alkyloxybenzoic acids (8OBA) with SWCNT: 8OBA/SWCNT. In our previous studies [12] we found that for most of the SWCNT concentrations used, new chiral phases were produced and, for some specific values of cell thickness and anchoring energy, the new unique smectic C\textsubscript{G} phase was induced. Now, we check the effect of nanotubes functionalized by carboxylic (COOH) groups (SWCNT-f). Furthermore, in the search for an adequate molecular and macroscopic model of the induction of the smectic C\textsubscript{G} phase, our results elucidate the interactions of 8OBA with nonmesogens like SWCNT regarding the compatibility and thermal stability of the nanocomposites.

2. Experimental results and discussion

The experiments were carried out on the nanocomposites 8OBA/SWCNT and 8OBA/SWCNT-f. For their preparation 3 mg SWCNT were mixed with 1.8 g 8OBA. For the mixtures pristine and COOH-functionalized SWCNT (SWCNT-f) were used. The nanotubes were produced by Catalyzed Chemical Vapor Deposition with the following characteristics: Amorphous Carbon Content: < 3 wt%; Length: 5-30µm; Specific Surface Area: 407 m\textsuperscript{2}/g; Electrical Conductivity: >100 S/cm; Bulk density: 0.14 g/cm\textsuperscript{3}; True density: ~2.1 g/cm\textsuperscript{3}. COOH-SWCNT contained 2.7% COOH groups.
The phases of achiral (pristine) 8OBA are isotropic (I), nematic (N), smectic C (Sc) and Crystal (Cr) (see table 1).

**Table 1.** Transition temperatures and enthalpies as determined by DSC for the phase transitions detected in the 8OBA, 8OBA/SWCNT and 8OBA/SWCNT-f.

|               | 8OBA     | 8OBA/SWCNT | 8OBA/SWCNT-f |
|---------------|----------|------------|--------------|
| T(°C)         | ΔH (kJmol⁻¹) | T(°C)     | ΔH (kJmol⁻¹) | T(°C) | ΔH (kJmol⁻¹) |
| T(I-N)=141    | 3.2      | T(I-N)=140 | 2.4          | T(I-N)=139 | 2.75 |
| T(N-Sc)=100   | 1.4      | T(N-Sc)=98 | 1.1          | T(N-Sc)=95 | 0.7  |
| T(Sc-Cr)=89   | 13       | T(Id'-Cr)=88 | 10.6        | T(Id'-Cr)=87 | 10.9 |

The thermal behavior of 8OBA/SWCNT and 8OBA/SWCNT-f was examined by differential scanning calorimetry (DSC) and the results are presented in table 1. The two nanocomposites display enantiotropic phase formation. The thermal scans were recorded in both endo and exo regime. However, we base our thermal analysis and the corresponding comparisons mainly on the exo thermograms. The endo scanning was used to study the hysteresis of the first order phase transitions. An example of the thermal scanning is shown in figure 1.

![Figure 1](image_url) **Figure 1.** The DSC scans of 8OBA, 8OBA/SWCNT and 8OBA/SWCNT-f.

Using the results of the table 1, one can complete the microtexture polarization analysis, directed to the building of a qualitative model of achiral-chiral transition in 8OBA/SWCNT and 8OBA/SWCNT-f nanocomposites.

The initial liquid crystal cell (LCC) with thickness d was homogeneously orientated. The surface orientation treatment is done by usual unidirectional rubbing of the ITO layer deposited on the substrates. In figure 2 the isotropic-nematic phase transition for 8OBA/SWCNT and 8OBA/SWCNT-f marked as I-N in table 1 is presented. As is seen, the LC growth in 8OBA/SWCNT (figure 2(a)) starts by modified Maltus crosses indicating quasi-homeotropic orientation in normal N, while that of 8OBA/SWCNT-f (figure 2(b)) arises with bifocal droplets typical for the chiral states, which exist for less than one °C and then readily transform in normal nematic N. Further consecutive cooling initiates a cascade of phase transitions for both nanocomposites, capturing chiral and reentrant phases, as
follows: $N \rightarrow$ chiral nematic ($N^*$); $N^* \rightarrow$ chiral smectic C ($S^*_C$); $S^*_C \rightarrow$ reentrant $N^*(N_{r}^*)$; $N_{r}^* \rightarrow C_G$ and $C_G \rightarrow$ Cr.

Figure 2. Textures of isotropic-nematic phase transition in unidirectionally oriented LC cells with $d=8 \mu$m of: (a) 8OBA/SWCNT at $T=140 \degree C$. (b) 8OBA/ SWCNT-f at $T=139 \degree C$.

For clarity, we present the microtextures of these phases of 8OBA/SWCNT-f in figure 3. The nanocomposite enters at $95^\circ C$ into a chiral smectic C ($S^*_C$) phase (in figure 3(a) the transition $N \rightarrow S^*_C$ is depicted). The textures $S^*_C$ are characterized by typical stripes indicating the helix direction. Upon further cooling, at $93^\circ C$ a reentrant chiral nematic ($N_{r}^*$) phase is reached. Figure 3(b) presents the $N_{r}^*$ texture. At $87^\circ C$ we observe a transition from $N_{r}^*$ to $C_G$ (figure 3(c)). Finally, at $55^\circ C$ a paramorphic solid Cr phase forms (figure 3(c)).

We identify the $C_G$ formation by the existence of a permanent out-of-layer electric polarization $P_{out}$ in this phase (for more details see [12]). This can be demonstrated with an electric field applied along the LC cell normal. Such application of electric field induces a second order phase transition $C_G \rightarrow C^*$ and further phase transitions to the I phase. The same phase transition can thus be a consequence of electric-field application, or temperature increase, or change in the enthalpy of the system. The requirement $\text{div} P=0$ [15] in this case allows the detection and calculation of the polarization $P_{out}$ by the modified Kirkwood-Helfrich equation. The polarization value calculation and electric field response of this phase, using the pyro-electric and triangular dielectric methods (see the details in [12,15]), will be presented in a future work. As seen from table 1, for the two nanocomposites 8OBA/SWCNT and 8OBA/SWCNT-f the phase transition temperatures gradually decrease which is mostly pronounced for the I-N or I-$N^*$ transitions.

Comparison of the microtexture temperature analysis with that of DSC scanning (see table 1) demonstrates that not each of the observed textural transitions is matched by a corresponding DSC peak. This indicates that some of these transitions, e.g. the $N \rightarrow N^*$, or the $S^*_C \rightarrow N_{r}^*$ ones are very weak resembling second-order transitions, while others ($N^* \rightarrow S^*_C$, $N_{r}^* \rightarrow C_G$) categorically display first-order behavior.

To calculate the anchoring energy $W_i$ in the N phase we measured the topological-defects (Neel walls) width $l$ and using the formula $W_i=\pi Kd/2l^2$ [13,15], where $K$ is the elastic constant ($10^{-11}$ J m$^{-1}$) taken in the one-constant approximation [15], we found the surface energy values for the investigated different samples: $0.2\times10^{-5}$ J m$^{-2}$ (8OBA), $0.15\times10^{-5}$ J m$^{-2}$ (8OBA/SWCNT) and $0.1\times10^{-5}$ J m$^{-2}$ (8OBA/SWCNT-f). The surface energy variation from $0.2\times10^{-5}$ J m$^{-2}$ (8OBA) through $0.15\times10^{-5}$ J m$^{-2}$ (8OBA/SWCNT) to $0.1\times10^{-5}$ J m$^{-2}$ (8OBA/SWCNT-f) indicates that the surface anchoring reduction in (8OBA/SWCNT and (8OBA/SWCNT-f) could take place at the expense of bulk ordering increase due to the conformability between the SWCNT-f and the 8OBA molecules. To explain this unexpected effect we propose a physical mechanism of the interaction between the molecules of...
8OBA and the functionalized SWCNT, including interaction with the orienting ITO surface. Surface functionalization helps in stabilizing the dispersion, since it can prevent re-aggregation of nanotubes and also leads to coupling of SWCNT with the LC matrix. Coupling between SWCNT and the LC matrix is also very important for efficient transfer of external stress to the nanotubes. As SWCNT have some surface defects like varying diameter and bends/twists due to non-hexagonal defects, mechanical interlocking plays a role in SWCNT–LC adhesion along a SWCNT. The chemical bond, either ionic or covalent, significantly improves the interfacial interaction between matrix and filler that enables a stress transfer. The van der Waals interaction also arises from the molecular proximity and is the only mode of interaction between SWCNT and the matrix in absence of chemical bonding. Although chemical functionalization of SWCNT can improve the compatibility between SWCNT and LC, which in turn improves the mechanical properties, it may deteriorate other properties of the nanocomposites near to the surface such as electrical conductivity and increase the stability of the electrical double layer reinforcing the surface pre-tilt and decreasing the anchoring strength. This effect could be interesting for the flexo-electric response of the LC system, where strong bulk ordering and weak surface anchoring are necessary. However, for other electro-optical phenomena, where a strong anchoring is needed, a preliminary deposition of oriented SWCNT on the orienting LCC surface can be performed, as was demonstrated in [13].

Figure 3. 8OBA/SWCNT-f textures in unidirectionally oriented LC cell with d = 8 μm: (a) Phase transition N → S∗ C at T = 95 °C. (b) N∗ r phase at T = 93 °C. (c) Cα phase at T = 87 °C. (d) Cr phase at T = 55 °C.

The chiral smectic C phase in 8OBA/SWCNT-f grows in well formed chiral lines (figure 3a) allowing control of the chiral axis and pitch value measurements. This effect and the transition to the
low-temperature smectic C₆ demonstrate the symmetry degradation from C₂ to C₁ as was shown in [12].

3. Conclusion
Using an optimal mixture of 8OBA with pristine and COOH-functionalized single wall carbon nanotubes (with respect to the concentration), we detect a process of chiralization of the otherwise achiral 8OBA in its pure state. The functionalized SWCNT weakly decrease the surface anchoring, but favourize the bulk ordering and the process of chiralization. The decrease of the phase transition temperature in the functionalized nanocomposite facilitates the desired effect in chiral ferroelectric liquid crystal materials concerning the isotropic-cholesteric phase transition temperature decrease. The linear decrease of the isotropic transition temperature upon electric field increase, which is equivalent to enthalpy variation, indicates a coupling of the induced out-of-layer plane polarization to the applied electric field.

Acknowledgments
This study was supported by Grant BK-04-14 from the Institute of Solid State Physics, Bulgarian Academy of Sciences.

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