Optical properties of dimeric liquid crystals doped with single-walled carbon nanotubes

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Abstract. Well oriented distinct local single crystals were grown in smectic C liquid crystal (LC) (heptyloxybenzoic acid - 7OBA) using predefined orientation of the single-walled carbon nanotubes (SWCNT). The SWCNT/SiOx/ITO/glass surface is found to cause a substantial enlargement of the smectic C distinct local single crystals and to reinforce both surface memory effect and surface anchoring. We synthesized and examined a set of nanocomposites, built of LC with hydrogen-bonded in dimers molecules (7OBA) and SWCNT. We found that the surface orientation strength and the interaction of the dimeric molecules with the carbon nanotubes play a decisive role for the type (symmetry), thermal stability and chirality of the LC states induced in the nanocomposites. As a result, a set of phase transitions and new phases (chiral smectic C, reentrant nematic, reentrant chiral nematic and a unique low-temperature chiral biaxial fluid smectic phase C生物质) not typical for pristine 7OBA were found.

1. Introduction

In the last few years, a wide range of nanosize materials have been the subject of current research due to their interesting properties and technological applications. Nanomaterial as a guest, in liquid crystals (LC) material may open a new era for the LC based display devices because of their unique structural, electrical and mechanical properties [1]. The proper selection of nanomaterials, concentration, homogeneity and their compatibility with liquid crystals show a remarkable impact on structural, switching, optical and dielectric properties of LC. Much of the works were focused on the dispersion of carbon nanotubes in liquid crystals for lower threshold voltage, faster switching time and better optical responses [2,3]. Single walled carbon nanotubes (SWCNT) show high conductivity along the tube length and are also known to align parallel to each other in low concentration solutions. These spontaneous self-alignment properties of SWCNT make them an attractive alternative for surface and bulk alignment in LC. It was indicated that the trapping of ions, present as impurities in any LC material, due to attracting of those to carbon nanotubes. Investigations of SWCNT as an alignment substrate for LC, as well as material for bulk orientation improvement were so far concentrated entirely on nematic and ferroelectric LC. Here we focus on the surface alignment of the smectic C (Sc) liquid crystals and on the bulk properties of mixture of SWCNT and nematics with short range smectic C order.
The goal of the present work is to further explore the anisotropy of SWCNT for formation of an oriented SC. As a second stage we study the optical and phase state properties of mixture SWCNT and nematics with short range SC order. In the two cases we used as a LC the seventh homologue of p-n-alkyloxybenzoic acids (7OBA), which characterizes with hydrogen bonded in dimers molecules.

SiO$_x$ layer, deposited on an ITO treated glass surface induces distinct local single crystals (DLSCs). We investigate its orientation, light polarization characteristics as well as their sizes. We also analyze the memorization strengths of these orienting substrates and compared them with those at SiO$_x$- and ITO- treated surfaces. We prepare mixtures of 7OBA with SWCNT in a wide range of concentrations and explore conditions for phase thermal stability, new phase induction, compatibility of the SWCNT with the nematic matrix, chirality and phase transitions in these nanocomposites.

To test the imposed by the SWCNT deposition surface orientation responsible for DLSCs texture enlargement and reinforcement of the memorization of an oriented SC texture in the temperature range of the N phase, known as surface memory effect (SME), we use spatially resolved polarized Raman spectroscopy [4,5]. Both the optical properties and phase states of the SWCNT treated LC cell surface and doped by SWCNT LC matrix we investigate by optical microtexture polarization analysis.

2. Experimental results and discussion
The experiments have been carried out with 4, n-heptyloxybenzoic acid (7OBA) which has following phase transitions:

\[
Cr \xrightarrow{92^\circ C} S_C \xrightarrow{98^\circ C} N \xrightarrow{146^\circ C} I
\]

Its chemical structure in dimeric form is demonstrated below:

\[
\begin{align*}
C_{12}H_{18} - O & \quad - O - H - O - C - O - H - O - C_{12}H_{18} \\
\end{align*}
\]

The LC material in its isotropic phase was filled in the cell using the capillary force action. The gap between the glass plates, defining a cell thickness of 20 μm, was maintained with Mylar spacers. The temperature of the sample was varied with a rate of 0.2 °C min$^{-1}$ by a hot stage temperature controller Linkam TMS 90, and the chosen experimental temperature was stabilized with an accuracy of ± 0.1°C.

A microscope Zeiss NU2 was used for the texture analysis.

The latent heat of 7OBA is 10.8 kJ.mol$^{-1}$. Under bulk or surface impact the closed dimers transform in open dimers or monomers. The most typical external influence causing such transformation is the temperature variation. As a result a peculiar temperature $T^* = 117^\circ C$ inside the N temperature range (98-146°C) exists for 7OBA, where a structural transition occurs [6]. Above $T^*$ the nematic behaviour resembles that of the ordinary nematics, while below this temperature strong smectic C fluctuations appear, thus forming nematic with short-range smectic C order.

Purified single-walled carbon nanotubes with diameters in the range 1.2 – 1.4 nm and an aspect ratio of 20 – 2000, assembled in thin bundles of > 2 μm length, produced by arc discharge at Hanhwa NanoTech Co. Ltd. have been used as purchased. The sonication and centrifugation procedure was applied to remove the big SWCNT agglomerates and most of metallic impurities. The remaining well dispersed SWCNT suspension in a form of droplet was placed on a series of substrates and blown with an air stream in the “rubbing” direction of the substrates until the solvent evaporated. This procedure pushes the suspension on the surface and leads to the self assembly of the SWCNT bundles along the blowing direction while the solvent evaporates, so that some alignment of the SWCNT is expected.

The Raman spectra were measured on a Jobin Yvon Labram spectrometer equipped with a CCD detector and entrance slits set to 1.5 cm$^{-1}$ spectral width. The 632.8 nm line of a He-Ne laser was used for excitation, the absolute accuracy being about 0.5 cm$^{-1}$. The laser beam with a power of about 1mW was focused on a spot of about 2 μm in diameter on the sample surface using microscope optics. In this way, a possible alignment of nanotubes lying on the sample surface should be detected due to the strong antenna-effect arising from the combination of a strongly resonant nature of the Raman effect in SCWNTs with the polarization effect due to the large nanotube aspect ratio, which renders the
Raman tensor approximately proportional to the polarizability tensor. This makes the resonance Raman signal from a carbon nanotube strongly orientation dependent. The scattering intensity of all Raman modes in a nanotube, regardless of their vibrational pattern, has then the same orientational dependence, approximately proportional to $\cos 4\alpha$, where $\alpha$ is the angle between the incident laser polarization and the nanotube axis. Thus the strongest signal is obtained when the laser polarization is parallel to the nanotube axis ($\alpha=0; \pm 180^\circ$), while the Raman intensity should nearly vanish for $\alpha=90^\circ$.

Spot-resolved measurement series performed as described above revealed an uniform orientational dependence of the intensity of all bands, as depicted in figure 1, with a period of $90^\circ$, closely resembling that of the function $\cos 2\alpha$ or $\cos 4\alpha$. We thus conclude that the SWCNT deposited on the SiO$_x$/ITO/glass surface have indeed a preferred orientation which can be determined with polarized Raman spectroscopy.

![Figure 1. Spatially resolved polarized Raman spectra at various orientation angles $\alpha$.](image)

Starting from the isotropic phase with very slow cooling, we performed consecutive growth of a planar N phase, and upon further cooling in the temperature interval between 92 and 98°C, we obtained a S$_C$ phase, containing DLSCs. Such DLSCs texture grown at 96.5°C on SWCNT/SiO$_x$/ITO/glass surface is presented in figure 2(a). As seen from this figure, the layers inside the black and white single crystals are directed at $\pm 45^\circ$ with respect to the horizontal direction. From observations by crossed polarizers we found these layers to be optically equivalent showing the same four extinction positions upon turning the sample by $2\pi$, allowing us to depict the S$_C$ layers topology (figure 2(b)): due to the imposed ‘easy’ direction in the $xy$ plane, the smectic layers follow $\pm 45^\circ$ directions, the projections of the tilted molecules being parallel to the $n_x$ axis. The inset shows a S$_C$ layer with a normal $N$ and a cone (formed by the tilt angle $\omega=45^\circ$) expressing the rotation around $N$ of the director $n$ (or equivalently the smectic C director $c$), thus minimizing the free energy of the system. Well ordered and enlarged (with average spatial lateral extent of the single crystals $\approx 0.2\text{mm}^2$) DLSCs are formed with surface anchoring, provided by the SWCNT/SiO$_x$/ITO/glass surface. For comparison, the sizes of DLSCs grown on SiO$_x$ or ITO/glass surfaces are 0.1 and 0.08mm$^2$ respectively. We assume that this enlargement of the DLSCs results from a decrease of the deviation of $n_x$ from the “easy” direction, forcing $\varphi$ to tend to zero, thus improving the bulk orientation.
We verify the ability of the SWCNT/SiOx/ITO/glass surface to reinforce surface anchoring and SME strength accordingly. The following memorization procedure is applied: we keep the cell at \( T_{rec} = 96.5^\circ C \) for the recording time \( t_{rec} \) to achieve an imprint of the SC texture like the one shown in figure 2(a) on the SWCNT-coated surface. Then we heat the cell up to a sufficiently high temperature \( T_{er} \) in the N state, to prevent emerging of any SC precursors. Even at this high temperature, the recorded DLSC-texture imprint still imposes its shape on the N-phase volume thus temporarily maintaining a similar texture in the N phase. Then we apply static erasure through annealing by keeping the cell at \( T_{er} \), for the so-called erasure time \( t_{er} \), during which the memorized SC texture is extinguished. In our experiment, the recording time was fixed at \( t_{rec} = 3\text{min} \) and the achieved erasure time for \( T_{er} = 135^\circ C \), was 150 min. To gain more insight in SME mechanism, we prefer static erasure through annealing as described above. The SME-imprint on the SWCNT-coated surface results from a reorientation of the LC molecules in the surface monolayer induced by the bulk LC alignment in the SC phase. Within the rotational diffusion model [7], the reorientation of the molecules in this monolayer, at recording and erasure, can be viewed as jumping over potential barriers between the local wells in conditions of reversibility of the SME. This can be approximated with an exponential Arrhenius equation \[ t_{er} = \tau \exp[-Q/(k_BT)] \]. Here \( Q \) is an energy barrier, which has to be surpassed by the thermal activation \( k_BT \) for effective destruction of the picture through rotational diffusion during a time interval \( t_{er} \) and \( \tau \) is an extrapolation parameter. The dependence \( \ln t_{er}(T^{-1}) \) is linear, and from the curve slope we calculate the erasure activation energy \( Q \). We have also measured the erasure time \( t_{er} \) of the DLSC texture as a function of the temperature.

The obtained values of \( Q \) for the three orienting surfaces: SWCNT/SiOx/ITO/glass, SiOx/ITO/glass and ITO/glass respectively are 470 kJ mol\(^{-1}\), 192 kJ mol\(^{-1}\) and 160 kJ mol\(^{-1}\).

Further we study the bulk action of the SWCNT, but using the most popular surface orientation - ITO/glass suitably rubbed. The important point now is the preparation of the compatible SWCNT/LC mixtures. For preparation of a composite 0.6 mg SWCNT powder was mixed in a mortar with 620 mg of 7OBA during heating. After some technological procedures a homogeneous gray powder has been obtained.

The prepared SWCNT/7OBA mixture was examined to check the existence of LC states starting with SWCNT concentration of 0.1 weight %. Such concentration does not display LC phase. The most general inference at mixing is: varying the concentrations and the type of surface influence (non-oriented or oriented LC cells) we can obtain new phases, which have not been observed until now in the pristine 7OBA.

Richer variety of phases is observed at SWCNT concentration of 0.01 weight % in a LC cell with \( d = 8\mu m \): after forming a chiral N (N\(^*\)) at 142°C, the system enters at 93°C into a chiral smectic C (Sc\(^*\))
phase (in figure 3(a) the texture of $S^*_C$ is depicted). The $S^*_C$ texture is characterized by the 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 $90^\circ C$ the reentrant chiral nematic ($N^*_r$) phase is reached. At $86^\circ C$ we observe a transition from $N^*_r$ to a low-temperature smectic phase (figure 3(b)), which is fluid (well indicated by small colored glass particles), not smooth, and colored in red and green mosaic domains, thus closely resembling the G phase [9,10], which is, as we will indicate by polarization analysis, a fluid biaxial smectic G ($C_G$).

**Figure 3.** The textures of 0.01 wt % SWCNT/7OBA in a LC cell with $d=8\mu$m: (a) Chiral smectic C at $T=91^\circ C$. (b) Low-temperature smectic phase $C_G$ at $T=86^\circ C$

Following the symmetry variation activated in the bulk by both thermal influence and by the interaction with the SWCNT, we find that the phase-transition and phase-stabilization sequence is as follows: the chiral $N^*$ starts immediately below the I phase and upon further cooling it turns into a $S^*_C$ (figure 3(a)), thus decreasing the symmetry to $C_2$ (twofold symmetry axis) and inducing an in layer’s plane polarization typical for the ferroelectric LCs. Yet further cooling brings the system into the reentrant chiral nematic state $N^*_r$, below which the system transforms to $C_G$ (figure 3(b)) and the symmetry decreases to the lowest possible one: $C_1$.

We focus on the smectic $C_G$ phase (see figure 3(b)). Applying a microtexture polarization analysis, we observe two red and green mosaic domains. We find that in crossed polarizers, upon sample rotation in either direction, the red color turns into green and vice versa. Furthermore, conventional chiral smectic phases are optically uniaxial because of their helix structure, whereas the $C_G$ phase observed here turned to be biaxial. To confirm this we perform special polarization analysis. The transition from $N^*_r$ is not only connected with a change in fluidity but also with the sudden appearance of birefringence (red and green colors) just below $92^\circ C$ and the texture loses its smoothness. From this we infer the biaxial nature of the $C_G$ phase, in contrast to conventional cholesterics and chiral $S^*_C$ which exhibit no change in color nor in intensity of the transmitted light upon rotating the film between crossed polarizers. Thus the phase observed here should be a $C_G$ biaxial fluid smectic phase. Certainly, this $C_G$ phase possesses a net permanent polarization and can be switched in a bistable way in an electric field which we plan to perform in future.

The anisotropic in-plane fluidity of $C_G$ (like that of achiral $S_C$ and unlike the smectic A, where this in-plane fluidity is isotropic) requires that none of the principle axes of the second rank tensor [13], characterizing the orientational order, to make an angle of $0^\circ$ or $90^\circ$ with the smectic layers planes. Thus, its polarization vector $P$, is tilted at an angle to the smectic layers. The polar vector now is expressed by its components $P(P_x, P_y, P_z)$. Its direction can not be determined by simple symmetry considerations. Also in contrast to $S^*_C$, $C_G$ has locally $C_1$ and globally $C_\infty$ symmetry. This implies that, unlike to $S^*_C$ the direction of macroscopic polarization is not fixed in a special symmetry direction (i.e.
there is no specific direction set by a mirror-plane or a twofold axis). Thus the $C_G$ is helielectric in the plane of its layers and ferroelectric perpendicular to them or it should be ferroelectric in the bulk.

3. Conclusion
A smectic C liquid crystal texture consisting of well oriented distinct local single crystals was grown using predefined orientation of the single-walled carbon nanotubes adsorbed on a SiO$_x$/ITO/glass surface. The SWCNT/SiO$_x$/ITO/glass surface is found to cause a substantial enlargement of the smectic C distinct local single crystals as compared to SiO$_x$/ITO/glass and ITO/glass surfaces. It was found that the surface memory effect and surface anchoring induced by the SWCNT/SiO$_x$/ITO/glass surface was many times stronger than those promoted by conventional SiO$_x$/ITO/glass and ITO/glass surfaces, normally used for liquid crystals orientation. We synthesized and examined a set of nanocomposites, built of liquid crystal with hydrogen-bonded dimers in its molecules (7OBA) and single-walled carbon nanotubes. We found that the surface orientation strength and the interaction of the dimeric molecules with the carbon nanotubes play a decisive role for the type (symmetry), thermal stability and chirality of the induced liquid crystal states (not typical for pristine 7OBA): chiral smectic C, reentrant nematic, reentrant chiral nematic and the unique low-temperature chiral biaxial fluid smectic phase $C_G$.

Acknowledgments
This study was supported by Grant BK-2/11 from the Institute of Solid State Physics, Bulgarian Academy of Sciences. The Korean Ministry of Education, Science and Technology is acknowledged for support from the World Class University Project (WCU, R32-2008-000-10082-0).

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