

# COMPOSITE WITH IMPROVED DISPERSION OF SINGLE WALLED CARBON NANOTUBES IN LIQUID CRYSTALLINE MOLECULES

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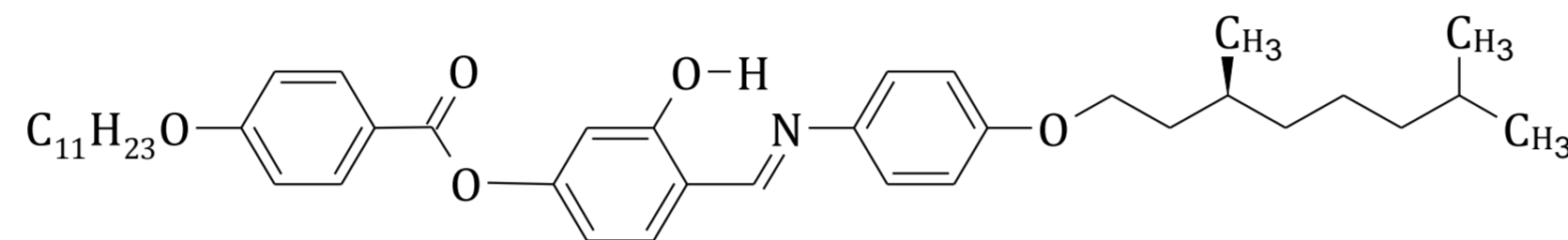
**Introduction:** Since their discovery in 1991, carbon nanotubes (CNTs) attract tremendous scientific interest. CNTs are nano-dimensional objects, possessing excellent electrical, optical and thermal properties, large area, and a broad temperature range of thermal stability, making them promising for environmental, electrical, optical, biomedical, and etc. applications<sup>1</sup>.

The main challenge to realize a successful CNT application is to achieve a homogeneous dispersion, since due to their very strong attraction they tend to re-aggregate and re-bundle<sup>2</sup>. Hence the stability of the CNT suspension is of great concern.

Different approaches have been adopted in resolving this issue. One pathway is to functionalize the CNTs<sup>2</sup> improving their solubility in liquid media. Unfortunately, introducing functional groups attached to the CNT surface leads to a change in some of the CNT excellent native properties. Another important issue is to find an appropriate solvent, taking into account the CNT hydrophobicity. Previous results show that polar organic molecules, such as DMF and NMP<sup>3,4</sup> are the best candidates but it still depends on the synthesis method and type of the CNTs. In addition, homogeneous dispersions are possible only at very low concentrations. Successful dispersing of CNTs has been claimed by polymer assistance<sup>4</sup>.

A new one promising concept is using liquid crystals (LCs). The main advantage of employing LCs is related to their long range orientational order that may help to disperse more effectively and even align the CNTs. Additionally, the properties of LC may enhance or modify those of the CNTs.

**Result and Discussion:** In the present study, a composite of single walled carbon nanotubes, SWCNTs (Meijo, Japan) and newly synthesized thermotropic liquid crystalline ((R,E)-4-(4-((3,7-dimethyloctyl) oxy) styryl) phenyl 4-(undecyloxy) benzoate)<sup>5</sup>, SB(3R)-11



was prepared from an ultrasonicated solution of NMP. As a result, the composite, after solvent evaporation, contained 1 wt. % SWCNTs. SB(3R)-11 is optically active chiral molecule.

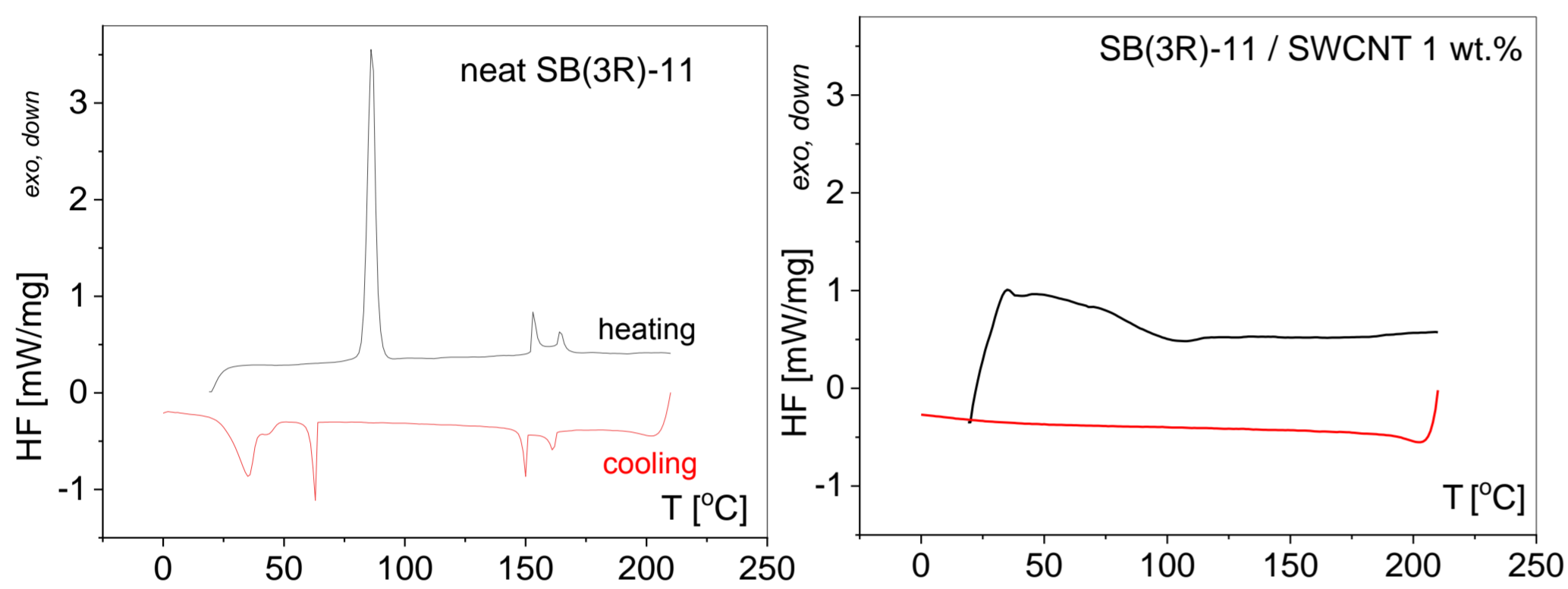


Fig. 1. DSC curves: neat SB(3R)-11 and nanocomposite; rate 10°C/min.

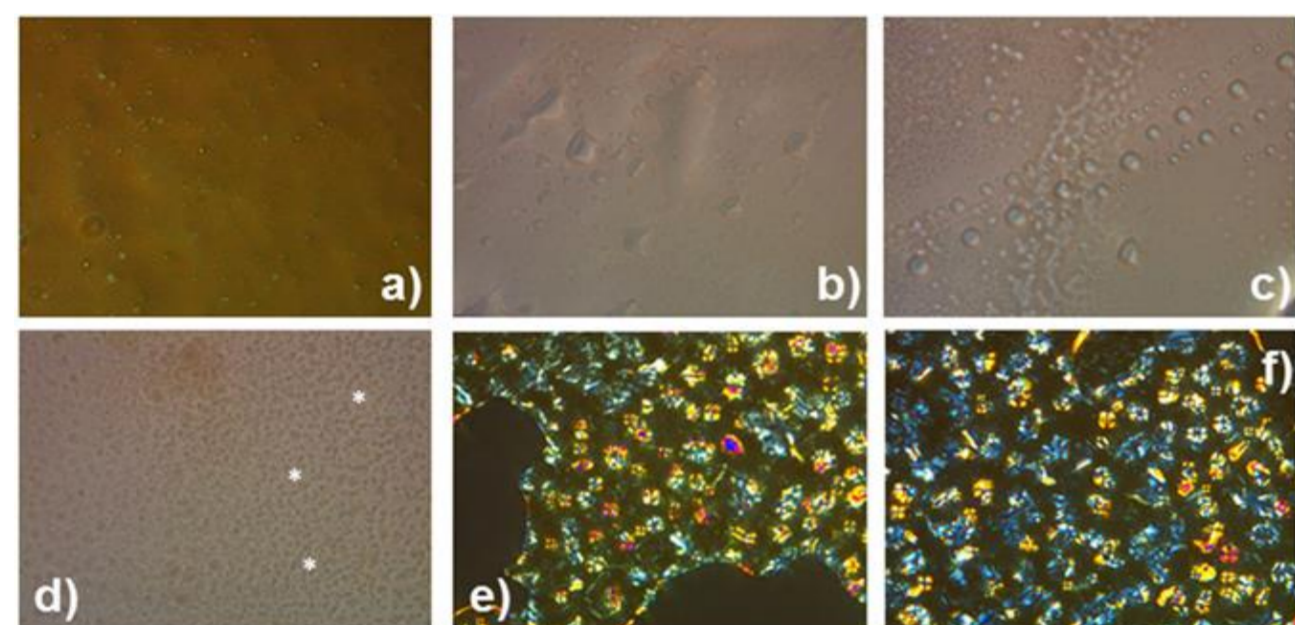


Fig. 2. POM of SB(3R)-11 (40x, Vh 5°C/min, Vc 0.2°C/min): a) at room temperature; b) heating, at 94.6°C - representative for the irregular drops formation; c) heating, at 117.5°C - regaining the circular drops; d) heating, at 184°C - the drops fill the entire field of view and a formation of the fiber-like entities from the colliding drops is also visible (see the apteryxes); e) at the end of the first heating-cooling cycle; f) at the end of the second heating-cooling cycle.



Fig.3. POM of nanocomposite (cross-polars, 40x, heating rate 5°C/min: a) at room temperature, the sample is as prepared; b) heating, at 92°C - the fibres melt; c) at subsequent cooling (0.2°C/min) - mixed texture consisting of fibre-like network and spherical coloured domains.

In Fig.1 the DSC heating and cooling curves for the neat SB(3R)-11 and for the composite are given. In the neat LC molecules clear consequence of phase transitions is seen. Previous examinations show that these are:  $Cr \rightarrow SmC^* \rightarrow N^* \rightarrow BP \rightarrow I$  in heating regime and  $I \rightarrow N^* \rightarrow SmC^* \rightarrow SmX \rightarrow Cr$  on subsequent cooling. Surprisingly, the nanocomposite show completely different behaviour. There are no clearly visible peaks on both cooling heating and cooling.

In order to understand the DSC results differences, POM at varying temperatures was performed, as seen in Fig.2 and Fig.3. Once again, the neat LC and the nanocomposite display different behavior. In the nanocomposite, even at room temperature, after the solvent evaporation, an interconnected network of fibers, shining in blue (Fig.3a) are clearly visible. This structure remains completely unchanged until almost 90°C (coinciding the DSC line

decrease). Then after, the fibers become wider and out of focus (Fig.3b), and disappear completely at about 97°C. On cooling, several phases are present simultaneously (Fig.3c). The final texture, yielded at room temperature show that the colored domains become less in number and smaller in size at the expenses of the fiber-like blue network. In general, the texture becomes more homogeneous. The general result is that the carbon nanotubes stabilize the LC structure in a very broad temperature interval (more than 60°C).

Comparing the DSC results, one has to conclude, that the LC phase behavior of the SB(3R)-11 was not lost in the nanocomposite. The lack of well-defined DSC peaks could be attributed to a structure, which had been formed jet in the solution. It might be a fibers with a core SWCNTs and a shell built up from LC molecules, attached to the tube surface. Then, the heating mainly improved the structure of those fibers. The remained free LC molecules adopt a phase, compatible with the confined space between the fibers. These local movement processes do not require much energy. The results can be interpreted as an improved dispersion of the nanotubes, since the LC shell of the newly formed fibers hinders the aggregation.

In order to prove this hypothesis, a Raman spectra of the nanocomposite was taken (Fig.4). The RBW mode of nanocomposites appears at lower Raman shifts, together with clear intensity rise of the band at 201  $cm^{-1}$ . Hence, the LC contributes to better dispersion of the SWCNTs. The G/D band ratio changes. It has a value of 12.36 for the pure SWCNTs and reduces here to 4.9. This ration is often used as a measure of the defects in the nanotubes and the change in the particular case is evidence, that the SWCNTs are bonded with the LC molecules. Moreover, such increase is typically observed for functionalized SWCNTs. Another proof of LC nanotubes interactions is the band broadening.

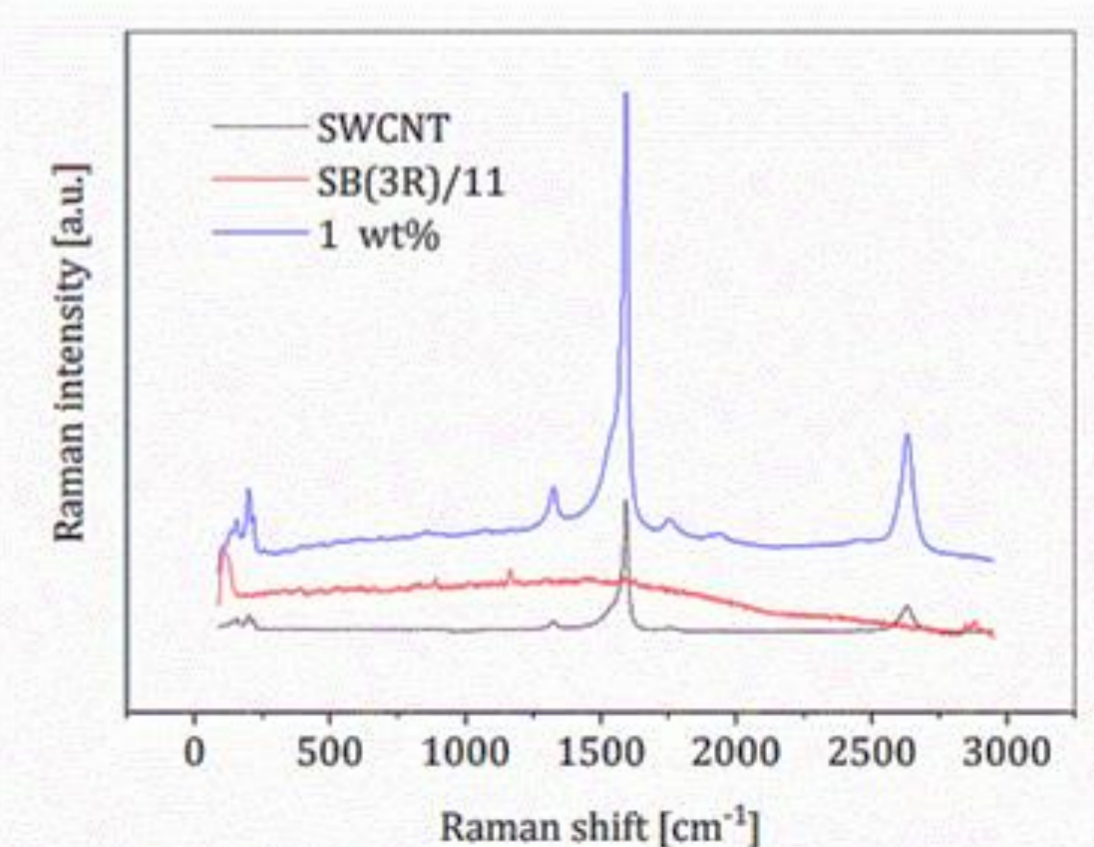


Fig.4 Raman spectra of SWCNTs, pure SB(3R)-11 and nanocomposite.

**Conclusion:** The results from DSC, Raman spectroscopy, and POM clearly show that the nanocomposite offers better SWCNTs dispersion. It is achieved by the core-shell fibers formation, where LC molecules are attachment onto nanotubes surface. The anchored molecules change the thermal behavior of the composite, but the LC behavior is still preserved.

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**Literature:** 1 N. Jain et al., Smart Sci. 10, 1 (2021)

2 D. Rajendran et al., J. Compos. Sci. 6(1), 26 (2022)

3 T. Premkumar et al., Small 8(9), 1299 (2012)

4 T. Hasan et al., J. Phys. Chem. C 112(51) 20227 (2008)

5 B. N. Veerabhadraswamy et al., New J. Chem. 39(3), 2011 (2015)