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Structural transitions in nematic liquid crystals doped with magnetite functionalized single walled carbon nanotubes

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Abstract

The 4-(trans-4'-n-hexylcyclohexyl)-isothiocyanatobenzene (6CHBT) nematic liquid crystal was doped with single walled carbon nanotubes (SWNTs) and with magnetite labeled single walled carbon nanotubes (SWNTs/Fe_3O_4). Prepared samples were characterized by infrared spectroscopy, transmission electron microscopy, optical microscopy and by magnetic measurements. Electric and magnetic Freedericksz transitions were measured for the pure liquid crystal, and for the liquid crystal doped with SWNTs, as well as with SWNTs/Fe_3O_4 (volume concentration $\phi = 10^{-4}$). The density of anchoring energy at the nematic–magnetic particle boundary was determined. The value of the anchoring energy density for SWNTs/Fe_3O_4 is lower than for SWNTs. The critical voltage of the Freedericksz transition depends significantly on the bias magnetic field.

Keywords: Liquid crystal; Fine magnetic particle; Ferronematics; Fredericksz transition; Anchoring

1. Introduction

Carbon nanotubes (CNTs) are materials with extra-ordinary physical properties relating to their mechanical, and especially to their electronic behavior [1]. Depending on their geometry, nanotubes can be metallic or semiconducting. These properties open a whole range of novel applications with devices envisioned in areas as diverse as nanoscale-electronics, field emission sources, actuators, nano-sensors, or even localized drug release at molecular dimensions. One of the basic pre-requisites for the employment of nanotubes in future nano-sized device applications is the ability to manipulate them with external electric and/or magnetic fields, or mechanically.

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Liquid crystals (LCs) are anisotropic fluids, thermodynamically located between isotropic liquids and three-dimensionally ordered crystals. They exhibit anisotropic physical, which in the case of thermotropic, calamitic (rod like) molecules induces orientational order of the long molecular axis along a preferred direction called the director ***n***. LCs can be oriented with magnetic or electric field due to their magnetic and electric anisotropies, however, the response of LCs to an external magnetic field is weak due to the small anisotropy of the diamagnetic susceptibility. In order to increase this response, Brochard and de Gennes [2] proposed doping LCs with fine magnetic particles, resulting in the so called ferronematics. Ferronematics are stable colloidal suspensions of fine magnetic particles in nematic LCs. The most essential feature of these systems is the orientational coupling between the magnetic particles and the liquid crystal matrix. The influences of the magnetic field depends on the density of anchoring energy, on the initial LC molecules orientation (***n***) with respect to the magnetic moment of magnetic particles (***m***), and on the size of the particles; since these parameters define the type of the anchoring.

In our previous work [3] we have studied thermotropic nematic 4-(trans-4'-n-hexylcyclo- hexyl)-isothiocyanatobenzene (6CHBT) liquid crystal doped with multi-walled nanotubes (MWNTs) and with magnetite labeled MWNTs. The obtained results have motivated us to study the same LC doped with single walled nanotubes (SWNTs) with the aim to generate a complex geometry of liquid crystal molecules with respect to nanoparticles. The first part of this paper is devoted to the preparation and characterization of magnetite labeled SWNTs (SWNTs/Fe_3O_4). In the second part we report the first results obtained on 6CHBT doped with SWNTs as well as with (SWNTs/Fe_3O_4) in regard of the influence of doping on the electric and magnetic Freedericksz transition.

2. Experiment

SWNTs and SWNTs functionalized with carboxy group were commercially available from Cheap Tubes Inc. They were produced by catalytic chemical vapor deposition (CCVD) technique and purchased as purified materials. SWNTs were of mixed chirality. About 60% of SWNTs were semiconducting and 40% were metallic. Their length ranged from 0.5 μm to 2 μm, outer diameter from 1 nm to 2 nm, inner diameter: 0.8-1.6nm. Other reagents ($FeCl_3.6H_2O$, $FeCl_2.4H_2O$, NH_4OH, HNO_3, and H_2SO_4) were of analytical grade. Magnetite labeled SWNTs were prepared by precipitation method in nitrogen atmosphere at 60°C.

Both pure SWNTs and SWNTs/Fe_3O_4 were characterized by a variety of methods, including infrared spectroscopy (Avatar 330 in the range from 400 to 4000 cm^{-1}. Magnetic properties of the products were obtained from magnetization measurements recorded by a SQUID magnetometer (Quantum Design MPMS 5XL). Transmission electron microscopy was employed to obtain structural and size information.

The 6CHBT liquid crystal was doped with prepared SWNTs and with SWNTs/Fe_3O_4, respectively, at a volume concentration of $\phi = 10^{-4}$. The doping was done by adding these particles, under continuous stirring, to the LC in the isotropic phase. The phase diagram of the mixture of 6CHBT and particles was obtained by polarizing microscopy. The calorimetric scans were performed by using a DSC instrument Mettler FP80HT in the temperature range from 20°C up to 90°C. No influence of the admixture of magnetic particles on the temperature of the nematic-to-isotropic transition has been observed. The electric and magnetic Freedericksz transitions were determined by capacitance measurements in a capacitor made of conductive ITO-coated glass electrodes. The external magnetic field was applied perpendicular to the surface of the electrodes while measuring the magnetic transition (Fig.1a). In measurements at combined electric and magnetic fields, the bias magnetic field was parallel to the surface of the electrodes and the electric field was perpendicular to it (Fig.1b). Before performing the measurements a high magnetic field (12 T) parallel with the surface of the electrodes was applied on all samples to align the nanotubes. The capacitor with the electrode area approximately 0.5 cm x 0.5 cm was placed into a thermostated system, in which the temperature was stabilized at 35°C with the accuracy of 0.05°C. The distance between the electrodes (sample thickness) was D = 5 μm. The capacitance was measured at the frequency of 1 kHz by the high precision capacitance bridge Andeen Hagerling.

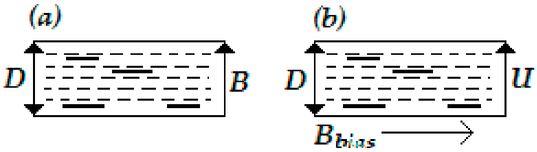

Fig. 1: The initial texture in the capacitor for classical magnetic Freedericksz transition (a), and for electric structural transition in a bias magnetic field (b). The thicker line represents SWNTs in 6CHBT.

3. Results and Discussion

Magnetic properties of the SWNTs and SWNTs/Fe_3O_4 were obtained from magnetization measurements. The saturation magnetization of SWNTs and SWNTs/Fe_3O_4 is 1.43 mT and 109 mT, respectively.

The classical magnetic Freedericksz transition was studied in the assumed experimental geometry shown in Fig.1a. For pure 6CHBT a threshold field of B_{cLC}= 3.34 T has been measured. The anisotropy of the diamagnetic susceptibility, $\chi_a = 3.10^{-7}$, has been calculated from the equation for the threshold field of the pure LC:

$$B_{cLC}{}^2 = \left(\frac{\pi}{D}\right)^2 \frac{\mu_0 K_1}{\chi_a}, \tag{1}$$

where D is the thickness of the LC layer and K_1 is the splay orientational–elastic Frank modulus.

In [4] it has been indicated that the axes of rod-like CNTs are aligned parallel to the LC directors and LC molecules are strongly anchored on the CNT wall, which is associated with the formation of helical wrapping to enhance hexagon–hexagon π-overlapping and charge transfer from LC molecule to CNT. The LC molecules anchored at the nanotubes should follow their movement. A formula for the change of the critical field in ferronematics can be obtained from the free energy of ferronematics [5]:

$$B_{cFN}{}^2 - B_{cLC}{}^2 = \frac{2\mu_0 W\phi}{\chi_a d}, \tag{2}$$

where B_{cFN} is the critical field of the magnetic Freedericksz transition of ferronematics, d is the typical particle size, ϕ is the volume concentration of the nanoparticles in the liquid crystal. Measuring B_{cFN}, from Eq. 2 the density of the anchoring energy W at the nematic–magnetic particle boundary was determined for 6CHBT+SWNTs as well as for 6CHBT+SWNTs /Fe_3O_4; the obtained values varied within the range of 6.75 – 27.0· 10^{-4} N m^{-1} and 4.03 – 16.1· 10^{-4} N m^{-1}, respectively. Note, that the density of anchoring energy for SWNTs/Fe_3O_4 is lower than that for SWNTs.

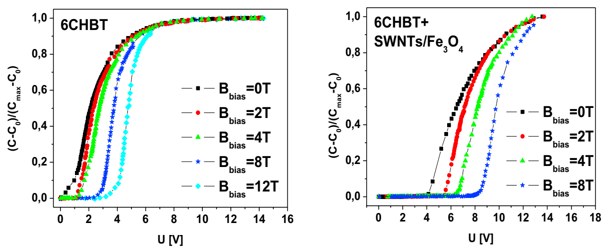

Fig. 2: The reduced capacitance dependence of 6CHBT and 6CHBT+SWNTs/Fe_3O_4 on external electrical field at different bias magnetic fields.

This fact is not surprising because the change of the critical field of the magnetic Freedericksz transition does not depend on the magnetic properties of added nanoparticles only on the density of anchoring energy.

In order to show that magnetic particles play an important role in the structural transitions, we have performed experiments in combined electric and magnetic fields too. The dependence of the reduced capacitance of 6CHBT and 6CHBT doped with SWNTs/Fe_3O_4 on external electric field in the presence of a stabilizing bias magnetic field is shown in Fig.2. The results are summarized in Fig.3. It is clearly seen that the behavior of 6CHBT doped with SWNTs does not differ significantly from that of he pure LC, while the strong influence of magnetite nanoparticles is immediately observable. The reason is that B_{bias} prefers to maintain the initial alignment of the LC molecules and the particles in the ferronematic, hence for their reorientation a higher electric field is necessary.

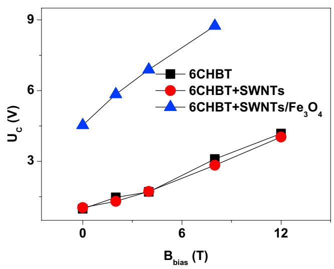

Fig. 3: The critical voltages U_C measured for different samples and magnetic fields.

4. Conclusions

The 6CHBT liquid crystal was doped with SWNTs and with SWNTs/Fe_3O_4. The electric and magnetic Freedericksz transitions were measured. The anchoring energy for different samples was calculated. It was shown, that the anchoring energy for SWNTs/Fe_3O_4 is lower than for pure SWNTs. The experiments in the presence of bias magnetic field showed a strong shift of the critical voltage due to fact, that the magnetization of SWNTs/Fe_3O_4 is about 70 times higher than that of the pure SWNTs.

Acknowledgements

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