Physica B 405 (2010) 4418–4423

Contents lists available at ScienceDirect

Physica B

journal homepage: www.elsevier.com/locate/physb

Dispersion of multi walled carbon nanotubes in a hydrogen bonded liquid crystal

V.N. Vijayakumar, M.L.N. Madhu Mohan *

Liquid Crystal Research Laboratory (LCRL), Bannari Amman Institute of Technology, Sathyamangalam 638 401, Tamilnadu, India

ARTICLE INFO

Article history:
Received 28 February 2010
Received in revised form
14 July 2010
Accepted 3 August 2010

Keywords:
Thermal properties
Optical properties
Permittivity
Doping effects
Carboxylic acids
Organic substances

ABSTRACT

In a newly synthesized self assembled system, namely, hydrogen bonded liquid crystal, multi walled carbon nanotubes (MWCNTs) are dispersed. This self assembly system of liquid crystal is realized by formation of hydrogen bond between levo tartaric acid and undecyloxy benzoic acid. The proposed structure is confirmed by FTIR and P-NMR studies. Thermal and electrical properties of this system dispersed with MWCNT are studied. Alignment of carbon nanotubes in the nematic phase of the self assembled system is responsible for the observation of bistable electrical states namely ON and OFF. Optical textural observations of these two states are recorded and the light intensity complexly decays and unwinding of the helix with the application of external field indicates an optical shuttering action. It is interesting to note that a small threshold value of 3.5 V/μm is sufficient to realize an optical shutter. DSC studied reveals that the enthalpy values pertaining to liquid crystal dispersed with MWCNT is approximately two fold to that of the pure liquid crystal. Results of conductance relating to the liquid crystal with MWCNT dispersion are discussed.

1. Introduction

Traditionally nematic liquid crystals are used for display device applications. With the advent of nanotechnology, to improve the electro optic characteristics of the liquid crystals, dispersion of carbon nanotubes (CNTs) in liquid crystals (LCs) are now widely studied [1–7]. A minute amount of CNT in the LC matrix leads to a major research area where the anisotropic properties of the LC can be investigated. The CNT dispersions are stable because they do not disturb the average direction of the LC molecules, which is referred as director field. The CNT alignment mechanism is governed by coupling of the unperturbed director field to the anisotropic interfacial tension of the CNTs in the nematic LC matrix, as individual CNTs are much thinner than the elastic penetration length [8]. Thus it is expected that the CNTs share the intrinsic properties with LC matrix [2].

With our previous experience in synthesis and characterization of various types of liquid crystals [9–24], in this present work we observe that addition of small amount of MWCNT to the liquid crystal has enhanced its optical and electrical properties. Furthermore an optical shuttering action in nematic phase is discussed.

2. Experimental

Self assembly system comprising of levo tartaric and undecyloxy benzoic acid, referred as LC, is synthesized as reported [20] earlier by us. The multi walled carbon nanotubes (MWCNTs) are available commercially [25] with an outer diameter <8 nm with typical lengths of 0.5 to 2 μm. A small amount (0.05 wt%) of MWCNT is dispersed in the liquid crystal and the resultant mixture in its isotropic state is ultrasonicated for 2 h so as to obtain mono dispersion of MWCNT without any aggregation. This mixture is referred as LC+MWCNT. Sonics Vibra Cell of 130 W (VCX 130 PB) is used for ultrasonic process. The mixture is degassed under vacuum at 35 °C for at least 1 h and is filled in a homogenous alignment liquid crystal cell [26] (5×5 mm^2 indium tin oxide coated area) of 4 μm spacing by capillary action. This LC cell is placed in a hot stage HCS 402 (Instec) where the temperature is monitored by a stand alone controller (STC 200) (Instec), which is interfaced to a computer and controlled by a Wintemp software program. The hot stage is placed under crossed polarizer of Nikon polarizing microscope for optical textural studies. Helicoidal measurements are made with the sample placed under crossed polarizers and an external electrical stimulus is applied to the liquid crystal in small increments of voltage. The optical setup reported earlier [16] comprises of a He–Ne laser, which is used as the optical source and the diffraction pattern is noted on the screen. Shimadzu DSC60 is used for obtaining transition temperatures and enthalpy values. Agilent 4192A LF impedance analyzer is used for measurement of

* Corresponding author. Tel.: +91 9442437480; fax: +91 4295 223 775.
E-mail address: mln.madhu@gmail.com (M.L.N. Madhu Mohan).

0921-4526/$ - see front matter © 2010 Elsevier B.V. All rights reserved.
doi:10.1016/j.physb.2010.08.006

the conductance of the sample. These hydrogen bonded complexes are analyzed using nuclear magnetic resonance spectroscopy (NMR) Brucker international model ULTRA SHIELD of 300 Mz. Infrared spectroscopy (FTIR) spectra is recorded (ABB FTIR MB 3000) and analyzed with MB 3000 software. All the chemicals used are supplied by Sigma Aldrich, Germany and all the solvents used were HPLC grade.

2.1. Synthesis of hydrogen bonded liquid crystal (HBLC)

The present intermolecular hydrogen bonded mesogen is synthesized by the addition of two moles of undecyloxy benzoic acids (11BA) with 1 mol of levo tartaric acid (LTA) in N, N-Dimethyl formamide (DMF), respectively. Further, it has been subjected to constant stirring for 10 h at ambient temperature of 30 °C till a white precipitate in a dense solution is formed. The white crystalline crude complexes so obtained by removing excess DMF are then recrystallized with dimethyl sulfoxide (DMSO) and the yield varied from 85% to 95%. The general molecular structure of the present homologous series of p-n-alkoxy benzoic acids with levo tartaric acid is depicted in Fig. 1, where *n* represents the alkoxy carbon number.

3. Results and discussion

3.1. Infrared spectroscopy (FTIR) and P-NMR studies

IR spectra of free p-n-alkoxy benzoic acid, levo tartaric acid and their intermolecular hydrogen bonded complex with MWCNT are recorded in the solid state (KBr) at room temperature. Fig. 2 illustrates the FTIR spectra of the hydrogen bonded complex of LC+MWCNT in solid state at room temperature. The solid state spectra of free alkoxy benzoic acid is reported [16–18] to have two sharp bands at 1685 and 1695 cm^{-1}, respectively, due to the frequency ν(C=O) mode. The doubling feature of this stretching mode confirms the dimeric nature of alkoxy benzoic acid at room temperature [16–18]. Further in the present LC+MWCNT hydrogen bonded complex a band appearing at 2924 cm^{-1} is assigned to ν(O–H) mode of the carboxylic acid group.

The doubling nature of ν(C=O) mode may be attributed to the dimeric nature of acid group at room temperature [16–18]. Corresponding spectrum of solution state (chloroform) shows a strong intense band suggesting the existence of monomeric form of benzoic acid. A noteworthy feature in the spectra of LC+MWCNT complex is the appearance of a broad band at 1674 cm^{-1} and nonappearance of the doubling nature of ν(C=O) mode of benzoic acid moiety. This clearly suggests that the dimeric nature of the benzoic acid dissociates and prefers to exist in a monomeric form upon complexation.

The proposed structure of LTA+nBAO complexes have been verified by P-NMR studies. As a representative case ^{1}H NMR for LTA+11BAO complex is discussed. NMR spectrum of the complex is recorded in $CDCl_3$ with TMS as the internal standard. The recorded spectrum is shown in Fig. 2(b) and the following chemical shifts are observed.

(a) Broad resonance signals are observed approximately in the range of 0.5–2.8 ppm for methylene group. In LTA+11BAO complex these signals are observed between 2.982 and 0.868 ppm, which are attributed to the existence of tacticity of backbone methylene.
(b) Two set of multiplets between 6.922–6.829 ppm and 8.006–7.914 ppm are equivalent to 2H and is attributed to aromatic protons.
(c) Existence of the methoxy proton unit resonance appears between 4.037 and 3.933 ppm.
(d) Methane group in the present complex is determined with the appearance of a peak at 4.500 ppm.

3.2. Phase identification

Molecular structure of liquid crystal under study is shown in Fig. 1 while the MWCNT is represented in Fig. 3. The observed

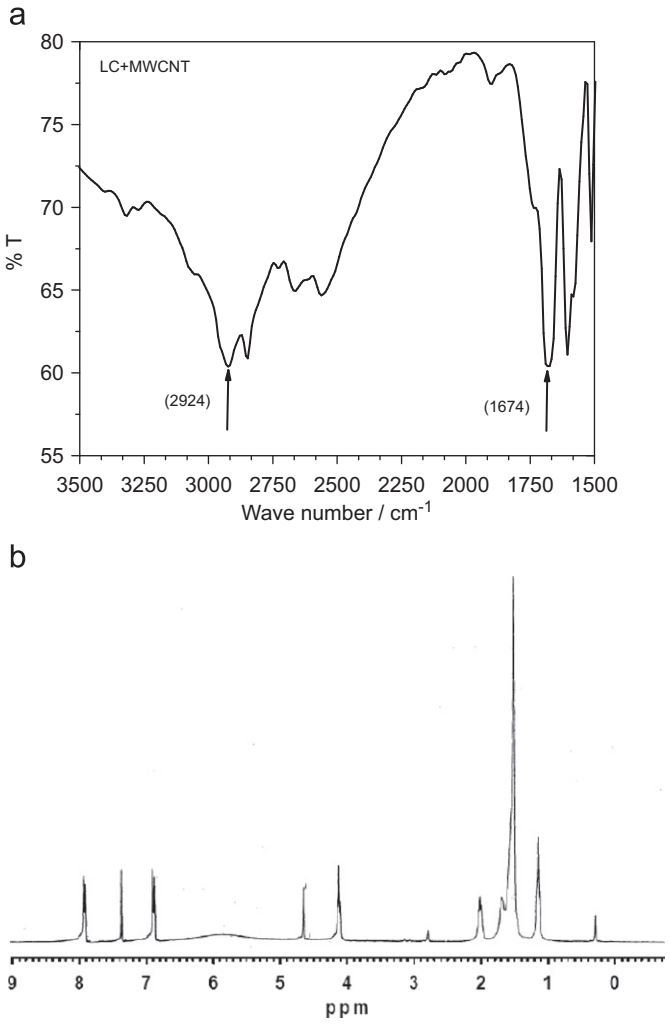

Fig. 2. (a) FTIR spectra of LC+MWCNT complex. (b) P-NMR spectra of LC complex.

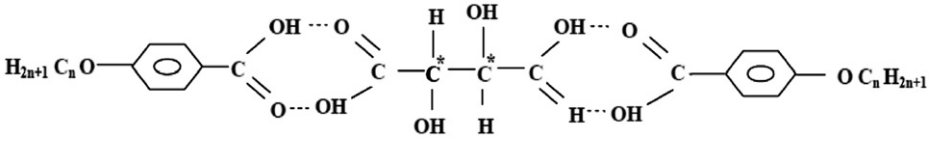

Fig. 1. Molecular structure of the hydrogen bonded liquid crystal.