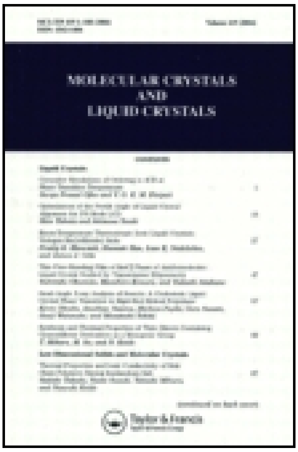

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Observation of Flexoelectricity in a Mixture of Carbon Single Walled Nanotubes with a Nematic Liquid Crystal

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Observation of Flexoelectricity in a Mixture of Carbon Single Walled Nanotubes with a Nematic Liquid Crystal

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We have measured the modulus of the flexo-surface polarization term: 5.1 pC/m for the case of the nematic E7. The extension of the theory of Helfrich for the case of flexoelectric bending-splaying of a nematic layer permitted to measure also the modulus of the flexoelectric sum: 15 pC/m. The inclusion of minute amounts of single-walled carbon nanotubes (SWCNTs) with a concentration below 10^{-3} wt. % changes the results obtained as follows: 14.7 pC/m and 78.7 pC/m, respectively. Additionally we have measured the value of the surface energy for the pure nematic E7 and the E7/SWCNTs mixture.

Keywords Flexoelectric bending; nematic E7; nematic-carbon nanotube interactions

1. Introduction

The discovery of the piezoelectricity (flexoelectricity) in the nematic liquid crystals began in 1969 with the famous theoretical prediction by Meyer [1]. Among the many flexoelectric effects discovered in nematics (see for instance the book by Pikin [2] and the review by Petrov [3]), a typical flexoelectric effect is the bending (splaying) of weakly anchored nematic in a transversal electric field (Fig. 1). The early observation of the bending of homeotropic MBBA (p-methoxy benzylidene p'-butyl aniline) in a transversal d.c. electric field had been made by Haas, Adams and Flannery [4]. Helfrich [5] first proved the flexoelectric nature of this bending by developing a simple theory, based on minimization of the electric enthalpy including the elastic, flexoelectric and dielectric energies. Schmidt, Schadt and Helfrich [6] reconsidered experimentally the bending of the nematic MBBA and estimated the value of the bend

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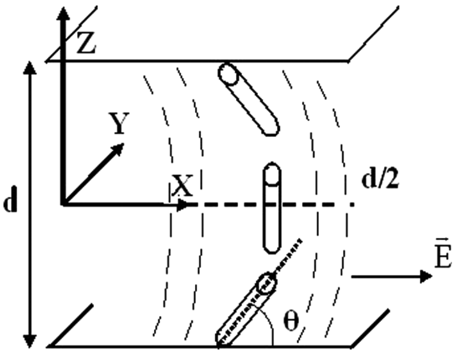

Figure 1. Schematic representation of the geometry of the liquid crystal cell and the flexoelectric bending of initially homeotroic nematic layer with minute amount of SWCNTs in a transversal electric field E.

flexoelectric coefficient e_{3x} (sometimes it is noted as e_3 or e_{33}) which is $|e_{3x}| = 1.23\,\mathrm{pC/m}$. It is important to stress that this flexoelectric effect can be obtained only in weakly anchored nematic (with maximum flexoelectric deformation at the interfaces). The second remark concerns the surface polarization (when the greater part of the nematic molecules is oriented at an interface in a polar manner) [7]. The measurement of splay flexoelectric coefficient e_{1z} (noted also e_1 or e_{11}) can be done with a similar method, but only in symmetrically weak-weak anchored planar (or tilted) nematic layer or in an asymmetrically strong-weak anchored planar layer. For instance, Hinov and Derzhanski performed such an experiment [8] and measured the value of the splay flexoelectric coefficient of MBBA. The flexoelectric behavior of mixture of two nematics, one of them several wt% has been also studied [9–11].

It is important to study the flexoelectric bending of a mixture of nematic and carbon nanotubes. The carbon nanotubes occur in two general morphologies: single-walled (SWCNTs) and multiwalled carbon nanotubes (MWCNTs) [12]. They are normally produced by the techniques of arc-discharge [13], chemical vapor deposition [14], or laser ablation [15]. The mixtures of liquid crystals and carbon nanotubes have been examined for the first time by Lynch and Patrick [16]. We could suggest that according to our knowledge there are no studies on the flexoelectric behaviour of such mixtures although many authors have studied the interactions between the liquid crystals, mainly the nematics, and the carbon nanotubes (see for instance the review papers [17] and [18]), including the Freedericksz transition, the electrohydrodynamics, etc. The E7/CNTS is the most intensively studied mixture. We have also studied this mixture. The aim of this study is to obtain the flexoelectric coefficient $(e_{3x} + m_p)$ by the well known method of Helfrich, where m_p is the surface polarization and the sum of the flexoelectric coefficients of splay and bend $(e_{1z} + e_{3x})$ of a mixture of the nematic E7 and a very small quantity noted as "trace amounts" or "minute amounts" of the single-walled carbon nanotubes, which in our case varies from 5.10^{-4} to 5.10^{-3} wt%.

2. Experimental Procedure: Materials, Technique Performance

We have used HiPco SWCNTs synthesized by decomposition of CO over Fe catalyst (the so-called gas-phase catalytic method) [18]. The SWCNTs are with average diameter around 1 nm and length of 1 μm. The nematic used is the well known eutectic liquid crystal (LC) mixture E7 with a positive dielectric anisotropy purchased from Merck Eurolab (Darmstadt, Germany) containing 51 wt% of 4-cyano-4′-n-pentyl-biphenyl (5CB), 25 wt% of 4-cyano-4′-n-heptyl biphenyl (7CB), 16 wt% of 4-cyano-4′-n-oxyoctyl-biphenyl (8OCB) and 8 wt% of 4-cyano-4″-n-pentyl-p-terphenyl (5CT) (the chemical formulae are shown in Fig. 2). The initial concentration of SWCNTs attempted by us was approximately 0.01 wt%. Usually, other authors use a concentration of SWCNTs in the nematic between 10^{-4} to 5.10^{-3} wt % [19–25]. Indeed, we became convinced that with a concentration of 0.01 wt% of SWCNTs we could not perform the experiment: drops (or clusters) and/or networks of clusters with sizes larger than 1 μm were formed [26–28] and distributed all over the greater part of the E7-SWCNTs cells. As noted by Chen and Lee [29] a dopant concentration higher than 0.05 wt% would cause CNTs to aggregate in the nematic solution. This problem is discussed in detail in the review by Rahman and Lee [18]. On the other hand, Scalia et al. [30] proved by Raman spectroscopy study that large SWCNTs bundles can drastically change the electro-optical properties of the nematic-SWCNTs mixture. In our case, the initial concentration of the SWCNTs (0.01 wt%) was diluted by several order of magnitude by adding more E7 and the dilution procedure has been used to achieve very dilute solution down to the interval 5.10^{-4} to 5.10^{-3} wt %. This work is focused mainly on the flexoelectric properties of the mixtures E7/SWCNTs. We saw under the polarizing microscope that the miscibility between the nematic E7 and SWCNTs with a concentration below 10^{-3} wt % was very good with exception of few bundles of SWCNTs. Furthermore, the transition temperature T_c, showing the nematic-isotropic phase transition, decreases slightly (60.1°C for the pure nematic E7 versus 59.8°C for the E7/SWCNTs mixture). Further, the dielectric anisotropy of the pure nematic E7 and of the E7/SWCNTs mixture has been measured in the possible

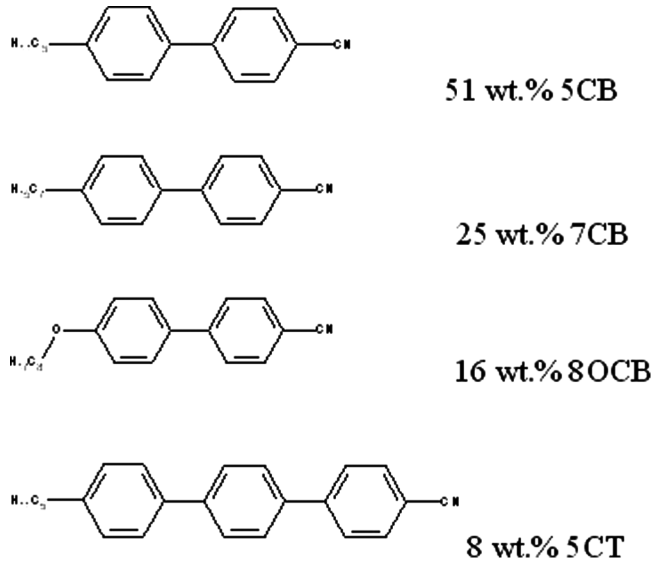

Figure 2. Schematic representation of the chemical formulae of the components which enter in the eutectic mixture of the liquid crystal E7.

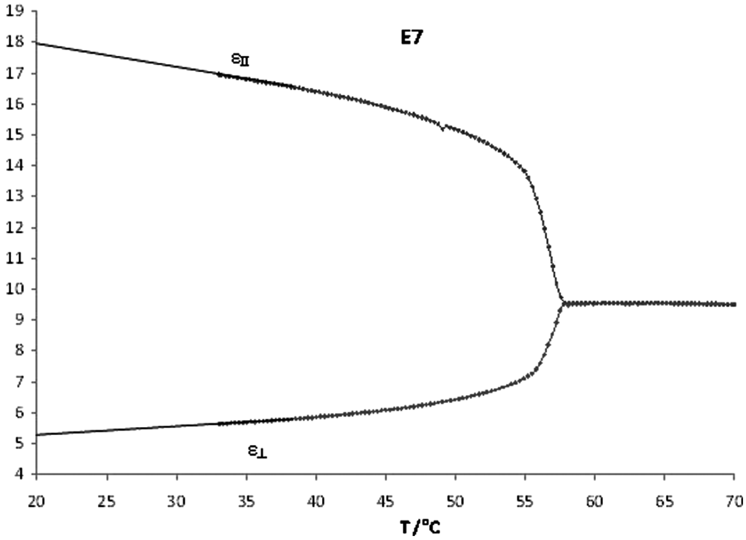

Figure 3. Measurements of the dielectric constants of the pure E7. Extrapolation of the curves up to room temperature (T = 20°C) is shown.

temperature interval (see Figs. 3 and 4). We make two clarifications: 1) T_c has been changed possibly due to impurity and 2) the curves have been extrapolated up to the room temperature (T = 20°C). One experimentally proves that the value of the dielectric anisotropy of the nematic E7 does not change at minute amount of the carbon nanotubes (cf. for instance [30]). The comparison of the value of the

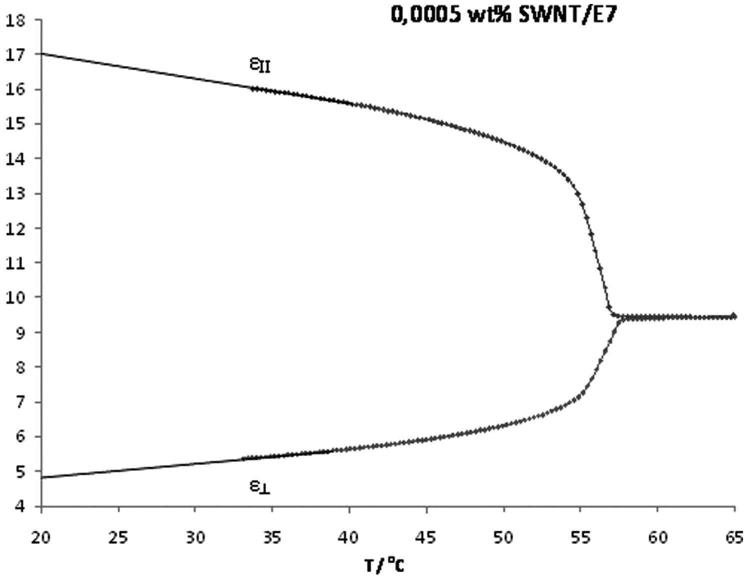

Figure 4. Measurements of the dielectric constants of the mixture 0.0005 wt% SWCNTs/E7. Extrapolation of the curves up to room temperature (T = 20°C) are shown.

two dielectric constants (perpendicular and parallel to the director) with those cited by other authors for the pure E7 [31,32] clearly shows that the change in $\varepsilon_{\|}$ is more significant which can be connected to the manner of the boundary preparation and the value of the surface energy of interaction between the molecules of the nematic E7 and the glass plates confining the liquid crystal [23]. Furthermore, the small amount of SWCNTs (below 10^{-3} wt %) does not change the value of the optical anisotropy Δn taken to be 0.2 at room temperature ($T_c = 20°C$) [32,33]. The elastic constants of bend K_{33} and splay K_{11} for the pure nematic E7 have also been measured [31,32]. The sum of the flexoelectric coefficients of splay and bend is available from refs [34]. and [35]. The difference between the same flexoelectric coefficients can be found in ref [36].

3. Theory

By generalization of the Helfrich's theory [5] for a stronger flexoelectric bending, an extended expression for the optical path of a nematic in a transversal electric field has been derived in ref [37]. Recently we have used a simplified version of this theory taking into account only the first correction Δ_1[11]. The corresponding expression for the optical path difference Δl is given below:

$$\Delta l = \left(\left(\frac{e_{3x} + m_p}{K_{33}}\right) E_{eff} \left(1 - \frac{(e_{1z} + e_{3x})(e_{3x} + m_p) d^2}{4K_{33}^2} E_{eff}^2\right)\right)^2 (n_e - n_0) \frac{d^3}{12}, \tag{1}$$

where

$$E_{eff}^2 = E^2 \left(1 + \frac{d}{2b} - \frac{\varepsilon_0 \Delta\varepsilon E^2 d^2}{12 K_{33}}\right)^{-2}, \quad \frac{\varepsilon_0 \Delta\varepsilon}{K_{33}} \frac{E^2 d^2}{12} = \frac{\pi^2}{12} \frac{d^2}{l^2} \left(\frac{U}{U_0}\right)^2. \tag{2}$$

Let us stress that the above formula is an approximation for smaller values of the electric field. The surface energy W_s can be calculating from the Freedericksz threshold for the case of a homeotropic nematic with weak anchoring under a transversal voltage [38]:

$$\cot \frac{\pi U_c}{2U_0} = \frac{\pi K_{33} U_c}{W_s d U_0}. \tag{3}$$

Expanding *cot* in a series and retaining the first two terms, finally we have obtained the following formula:

$$W_s = K_{33} \frac{\pi^2}{2d} \left(\frac{U_c}{U_0}\right)^2 \left[1 + \frac{\pi^2}{12} \left(\frac{U_c}{U_0}\right)^2\right] \tag{4}$$

for calculating the value of the surface energy with a sufficient accuracy. U_0 was calculated to be 32.9 V for $\Delta\varepsilon = 14$ at $T = 21°C$ [31]. The Freedericksz threshold has been measured by ac voltage with a frequency of 5 kHz. The conoscopic measurements clearly showed $U_c = 17$ V for the pure nematic E7 and $U_c = 22$ V for the mixture E7/SWCNTs. The calculations yield the following value for the surface energy: 0.4×10^{-6} J/m^2 for the case of pure nematic E7 and 0.78×10^{-6} J/m^2 for the E7/SWCNTs mixture.

4. Experimental Results

The LC cell was constructed with two glass plates covered by small quantity of lecithin to promote homeotropic orientation of the nematic (20 µM solution of lecithin in chloroform) and two cooper foils, 75 µm thick, posed on the glass plates which serve both as separating foils as well as electrodes. The distance between metal foils was measured to be 2 mm. We prepared two cells: pure E7 with a nematic-isotropic phase transition temperature T_c of 60.1°C and a mixture of E7/5.10^{-4} wt% SWCNTs with T_c of 59.8°C. The temperature was kept with electronic regulator and Mettler hot stage FP82 and indicated by precise electronic thermometer with an accuracy of 0.01°C. The optical observations and measurements were performed by the polarizing microscope MPI5 (Poland), either in transmitted light convenient for optical observations and for the performance of the experiment, or in the differential regime convenient for measuring the optical path difference. In this regime at appropriate disposition between the liquid crystal cell and the two polarizers (nicols), by means of special ocular and a long-distance objective (in our case × P3 × 0.10), one can see in a white light a dark interference fringe, which moves at the flexoelectric bending or bending-splaying of the nematic layer. By a microscope screw the interference fringe was returned in the initial position and thus the optical path difference Δl was measured by using the following relation: $l(E)\text{-}\ l(0) = \Delta p \lambda / h = \Delta p.0.550/2680$, where Δp is the measured shift of the dark fringe due to the electrically induced birefrigence, $\lambda = 0.550$ µm is the average wavelength of white light and $h = 2680$ µm is the distance between two successive dark fringes under white light illumination. The experimental points for the cell filled with pure E7 in the nematic phase at room temperature ($T_c = 21°$ C) as well as for the mixture E7/SWCNTs at the same temperature ($T_c = 21°$ C) are shown in Figure 4. The value of the experimental points clearly shows that there are 3 regions with respect to the value of E^2_{eff}: the first one relates with the influence of $(e_{3x} + m_p)$, the second one relates with $(e_{1z} + e_{3x})$ $(e_{3x} + m_{p)}$, and the third one relates with the dielectric reorientation of the director. Further, we are using only the first two regions which permit to evaluate $(e_{3x} + m_p)$ and $(e_{1z} + e_{3x})$. The fitting procedure according to the above shown formula has been performed very carefully (see Fig. 5). At the fitting procedure, the dielectric term in the relation for E^2_{eff} has been disregarded. The second term in this relation is connected with the anchoring of the nematic director with the glass plates treated with lecithin. The fitting procedure for the pure nematic E7 clearly showed that the term d/2b, where b is the extrapolation length introduced firstly by de Gennes, corresponds to 0,798 which means, as noted above, that the surface energy is 0.4×10^{-6} J/m^2, a completely reasonable value. The inclusion of the SWCNTs enlarge the term d/2b to 1.5 which means that the surface energy is enhanced up to 0.78×10^{-6} J/m^2. The fitting procedure of the first 4 experimental points with the theory clearly points out

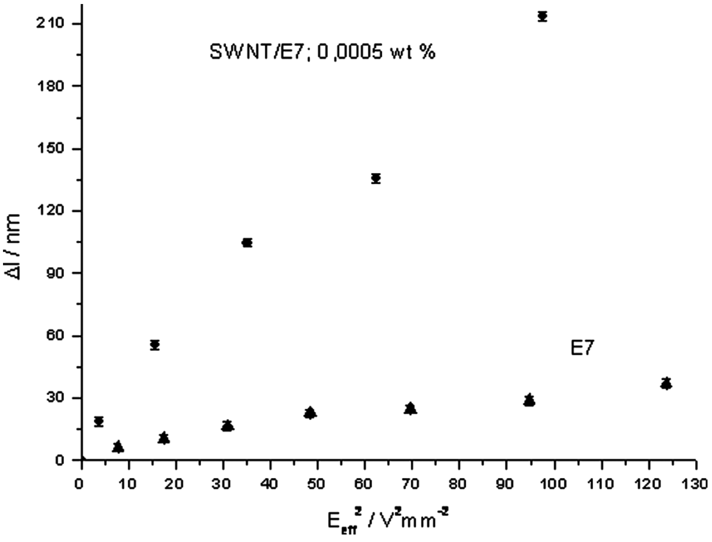

Figure 5. The optical path difference Δl in nm versus E_{eff}^2 in $(V/mm)^2$ of 75 μm thick nematic layer at room temperature (T = 21° C) for: a) pure E7 (triangles) and b) 0.0005 wt% SWCNTs/E7 mixture (circles). The absolute experimental error is ±2 nm.

the following absolute values for the term $|e_{3x} + m_p| = 5.1\,pC/m$ and the term $|e_{1z} + e_{3x}| = 15\,pC/m$ for the pure nematic E7 and $|e_{3x} + m_p| = 14.7\,pC/m$ and $|e_{1z} + e_{3x}| = 78.7\,pC/m$ for the case of E7/SWCNTs mixture, respectively.

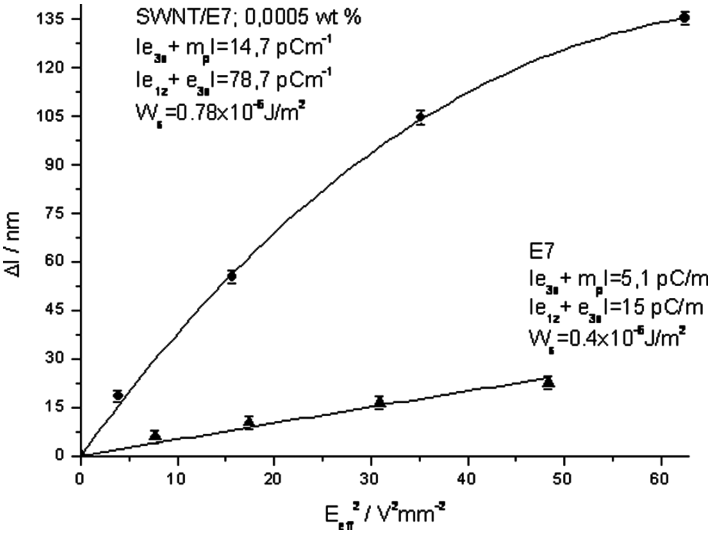

Figure 6. The Δl fitted curve in nm versus E_{eff}^2 in $(V/mm)^2$ for: a) pure nematic E7 (triangles) taking the following material parameter values: $\Delta n = 0.20$, $(d/2b) = 0.798$, $K_{33} = 19.13 \times 10^{-12}\,N$ (T = 21° C) and b) the mixture 0.0005 wt% SWCNTs/E7 (circles) taking the following material parameter values: $\Delta n = 0.20$, $(d/2b) = 1.5$, $K_{33} = 19.13 \times 10^{-12}\,N$ (T = 21°C). The absolute experimental error is ±2 nm.

5. Discussion and Conclusion

We will briefly discuss the influence of the nematic on the minute amount of SWCNTs and vise versa, the influence of the carbon nanotubes on the nematic molecules. There are several concepts for the nematic-SWCNTs interactions. The first one is connected with the coupling between the CNTs and the nematics by anisotropy surface tension domination [39] and not by any deformation of the director field because the rods are thin (several nanometers in diameter) to the scale of extrapolation, as experimentally observed first by Lynch and Patrick [16]. This idea is directly linked to the study of Shah et al. [40] on a flow of LC in CNTs with large diameters. Other experimental results are connected with the strong surface interaction between the nematic molecules with the phenyl rings persisting in some LCs and the surface of the CNTs [20,41,42]. It was experimentally proved [41] that the phenyl rings interact strongly with the graphene sheet of the nanotube surface through intermolecular overlap of π-orbitals (π-streching). The interaction energy was estimated to be close to $-2\,\mathrm{eV}$ [20]. The liquid crystals are also able to interact electrostatically forming surface charge transfer complexes with SWNTs. The excess charge induces a permanent dipole moment in the CNTs [43,44] which originates from the asymmetric LC molecular anchoring on CNT axis. Our conclusion for the interactions between the nematic and the isolated SWCNT's is that the carbon nanotubes follow the orientation of the nematic director. Accepting that the SWCNTs also affect the nematic we can conclude that the carbon nanotubes modify the orientation of the liquid crystal which diminishes its large anchoring energy. This influence is more pronounced with larger lengths of the carbon nanotubes. In this manner the minute amounts of the nanotubes enhance the flexoelectric response of the E7/SWCNTs mixture as is clearly shown by the experimental results.

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