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Synchrotron infrared microspectroscopy of nematic liquid crystals in polymeric micro cavities

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Liquid crystalline phases are typical examples of soft complex materials that exhibit interesting physical and chemical properties and that allow investigating an abundance of different physical phenomena. In this paper, we present experimental results that may contribute to better understanding the physics of confined states for nematic liquid crystalline materials. By using InfraRed Syncrotron Radiation (IRSR) and spectroscopic analyzing the FTIR spectra, we obtained information about the orientation for the nematic liquid crystal (NLC) molecules confined in pre-designed micrometric cavities, that were created on the surface of a polymeric film. By applying an electric field, the NLC molecules inside the micro structures and in the boundary areas were reoriented. The experimental results have been also compared with Monte Carlo simulations and confirm that micro and nano scale cavities have a significant influence on liquid crystals molecular orientation.

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1. Introduction

Lately, liquid crystalline (LC) materials and special confinement conditions have been extensively studied owing to the great significance for the liquid crystal display industry and various other application fields [1-5]. New materials and alignment techniques [6-12] have been developed and employed to study and better understand the phenomenon of orientation (and anchoring) of various liquid crystalline materials by the surface boundaries. Most of the research in the field was done by using nematic liquid crystals (NLC), because they posses the simplest known liquid-crystalline structure - the elongated rod-like molecules orient on average parallel to each other in the bulk. We can describe the macroscopic behavior of NLCs by using the unit vector field n(r) which is called “director”. n(r) represents the local average orientation for the long molecular axes [15]. At the surface, the alignment of the director is determined by the competition between surface, bulk interactions and possible external stimuli (mechanical, electrical, magnetical). These interactions have been the subject of rigorous analysis, whereas the surface anchoring strength was one of the highlights of theoretical and experimental investigations [16-18]. The structure of the liquid crystalline phase in close proximity to an interface is different from that in the bulk, and this behavior changes the boundary conditions and influences the director distribution in the volume. The nematic phase is especially sensitive to external agents, in particular, to surface forces.

Within confined systems, these properties are generally determined by the relative size of the space, the geometry, the order level induced by the surface and the generated disorder from external interactions. All the gathered synergic effects make a theoretical approach to be very difficult; therefore, the best choice is represented by an initial experimental characterization of the proposed system [2].

From this point of view, liquid crystals are perfect candidates for this study: they have a large variety of phases, chemical structures, interesting and special properties (viscosity, transparency, optical anisotropy etc) [19].

Typically, when building a liquid crystalline system, one uses a thin polymer film boundary surface condition. The reason is that the mesophase tends to follow the pre-imposed alignment dictated by the surface: it could be planar, homeotropical or tilted [15]. The potential technological applications emerge from the possibility of controlling the LC bulk orientation by placing several “control” centers (represented by micro cavities) on the surface [20,21].

2. Materials and methods

The sample was prepared between two optical polished ZnSe substrates (cca. 25 mm in diameter and 1mm thickness) that are transparent to both visible and IR radiations. Both substrates were coated with a thin conducting layer of indium tin oxide (ITO) of approximately 100 Å thickness. Subsequently, a PANI (polyaniline) or polyimide type thin polymer layer was deposited by means of the spincoating technique. In order to completely eliminate the solvent, the obtained polymeric films were then appropriately thermally treated. Following an EHD procedure [22], the initial planar surface of the thin polymer film was tailored to obtain a 2D structure of cavities. We have favored the use of a wedge-like geometry for our cell in order to avoid interferences. The employed liquid crystal was the nematic 5CB (4-pentyl-4'-cyanobiphenyl) from Merck. The filled cell was then fitted into a special sample holder designed for optical measurements. During the measurements we applied a maximum voltage 30V d.c. or a.c. at 1KHz. Information about the quality of the alignment and the apparent tilt angle of the molecular director in the micro structures were determined by using an optical polarizing microscope.

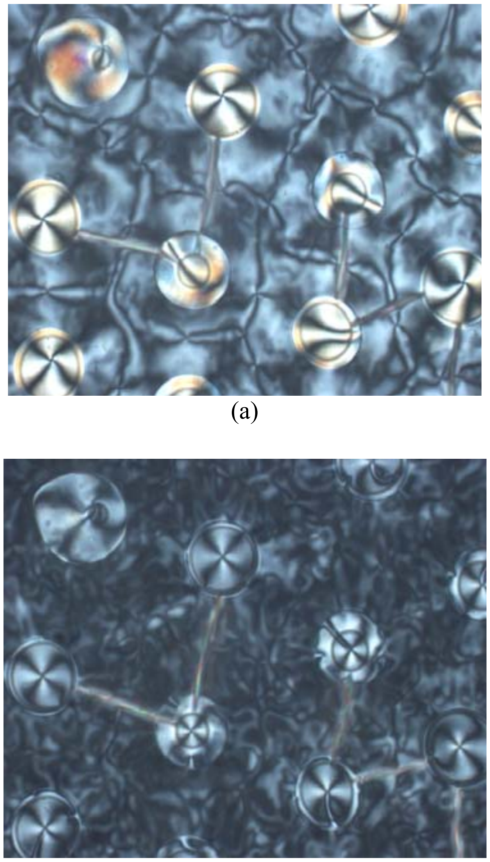
Spectral measurements were performed by means of a synchrotron IR beam, in the 650 to 4000 cm^{-1} (with a resolution of 2 cm^{-1}) wave-number range. The interferometer line included a Bruker Equinox interferometer, modified for vacuum operation, covering the range 10 – 12000 cm^{-1} (with a resolution of 0.5 cm^{-1}), equipped for both transmission and reflectance measurements with a MCT (mercury–cadmium–telluride) detector, and a Bruker microscope working in the range 400-8000 cm^{-1}, equipped with computer-controlled sample-scan stage, 3 IR objectives (4X, 15X, 32X) and adjustable diaphragms of 20 to 50 micrometers in the focal plane.

3. Experimental results and discussions

3.1. Optical microscopy

Optical microscopy measurements have revealed the formation of EHD patterns on the polymeric thin film surface due to the special electro-thermal treatment. Thermal fluctuations on the surfaces of the thin polymeric films can be amplified by the long-range van der Waals or dispersion force which act across the film. When polymeric films are heated, the EHD instability leads to the formation of singular or cluster cavities. When using these films as substrates for the anchoring of the NLC, the surface topology and, especially, its possible imperfections play an important role in inducing volume orientations of the symmetric or asymmetric LC cells [23].

The electro-optic response of the LC cell depends on the type of the used polymer as well as the polarity (+ or – on the polymer side) as shown in Fig. 1. One can also notice a different LC electro-optical response, depending on the investigated area: in the homeotropic region the LC response is uniform, whereas in the "cavities" it is slightly different. Our measurements for the anchoring energy at the LC-PANI interface show a value of about 5×10^{-4} J/m^2, which was obtained by photo-polarimetric investigations [17].



(a)

(b)

Fig. 1. Optical microscopy of an asymmetric cell (ITO\PANI\5CB\ITO), U=10V, f=1KHz. Size of the cavities is about 30 microns. (a) Positive polarity is on Polymer side; (b) Negative polarity is on Polymer side.

3.2. FTIR microscopy

In order to investigate the alignment of the nematic, firstly, we have to identify the polarization affinity of the LC molecules. Table 1 shows the polarization tendencies of each peak of the 5CB LC molecule as it was obtained from the FTIR spectroscopy (Fig. 2).

Table 1. FTIR peak assignment for 5CB liquid crystal [24-26].

Frequency	Mode
2957*	CH_3 antisymmetric C-H stretch
2926**	CH_2 antisymmetric C-H stretch
2870*	CH_3 symmetric C-H stretch
2857**	CH_2 symmetric C-H stretch
2226*	$C \equiv N$ stretch
1606*	phenyl C-C stretch
1494*	phenyl C-C stretch

* parallel transition moment tendency

** perpendicular transition moment tendency

By considering these results we can now characterize the orientation of the nematic LC molecules in the polymeric cavities.

For the LC molecules aligned parallel with the cavity main symmetry axis (i.e. normal to the ITO substrates), the peaks with a polarization tendency parallel to the molecular long axis, such as the –C≡N stretching at 2226 cm^{-1} (see Table 1), will illustrate a weak absorbance. On the contrary, the overtone peak at 1912 cm^{-1}, having a perpendicular polarization tendency, will show high absorbance.

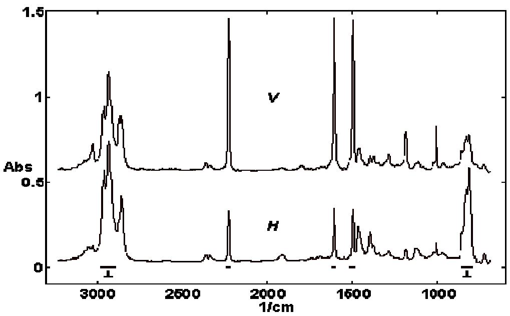


Fig. 2. FTIR spectroscopy diagram for the 5CB nematic liquid crystal (H is for planar horizontal polarization and V is for homeotropic normal polarization).

In the case the nematic rod like molecules align perpendicular to the main symmetry axis of the cavity (i.e. parallel to the ITO substrates), the reverse trend will occur: high absorbance peak for the –C≡N stretching at 2226 cm^{-1} and a weak one for the overtone at 1912 cm^{-1}. To determine the effect of the electric field on LC orientation in cavities and in their immediate vicinity we must calculate the respective dichroic ratios R from the equation:

$$R = \frac{A_{\perp}}{A_{\parallel}} \tag{1}$$

where $A_{\perp}$ is the area of the absorbance peak which designates perpendicular polarization tendency, and $A_{\parallel}$ is the area of the absorbance peak which denotes parallel polarization tendency. A larger dichroic ratio, R, indicates that, on average, more LC molecules are oriented parallel with the main symmetry axis of the cavity.

For estimating the dichroic ratio values, several peaks with suitable polarization tendencies can be considered. However, C–H region peaks from 3000 to 2800 cm^{-1} are difficult to read, due to the overlap of a potential new peak at 2897 cm^{-1} [24, 25]. We therefore decided to use the following peaks to measure the R values: one is the first overtone of the CH- out-of-plane deformation of the benzene CH groups at 1912 cm^{-1} and the other one is the –C≡N stretching peak at 2226 cm^{-1} (they denote perpendicular and parallel polarization tendencies, respectively). We have then measured the area of the overtone peak at 1912 cm^{-1} (1945.9–1890.9 cm^{-1} region) and the area of the –C≡N stretching peak at 2226 cm^{-1} (2250.0–2205.2 cm^{-1} region) and the results are presented in Fig. 3.

We have studied both radial and general homeotropic anchoring conditions for the NLC. Without the field, the NLC molecules tend to keep an arrangement that is perpendicular to the polymeric film surface (i.e. radial inside the micro cavities). The curvature of the surface imposes the presence of a distortion in the molecular field inside the cavity and in its immediate vicinity.FTIR microscopy measurements inside the cavities (that have the diameter comparable with the used microscope diaphragm) clearly indicate a decrease of the homeotropic orientation. General hometropic orientation of the LC molecules was revealed by FTIR microscopy and also by optical microscopy in polarized light when applying an electric field to our cell. The molecules inside the cavities and in the vicinity are reoriented (from radial to general homeotropic – i.e. normal to the ITO substrates).

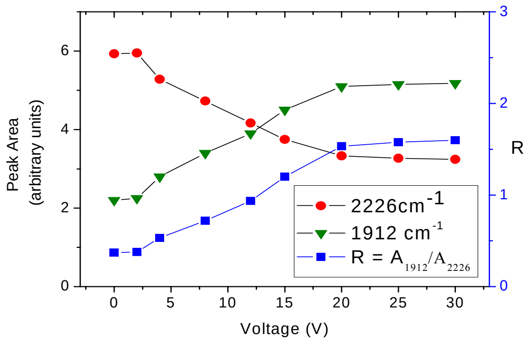


Fig. 3. The dependence on the applied voltage of the (green) area of the overtone peak at 1912 cm^{-1} , (red) stretching peak for the –C≡N at 2226 cm^{-1} and (blue) the dichroic ratio R.

In Fig. 4 we determined the dependence on the applied voltage of the area for the C≡N stretching peak at 2226 cm^{-1} (2205-2250 cm^{-1}). These results were also confirmed by the evolution of the 2928 cm^{-1**} and 2869 cm^{-1*} peaks.

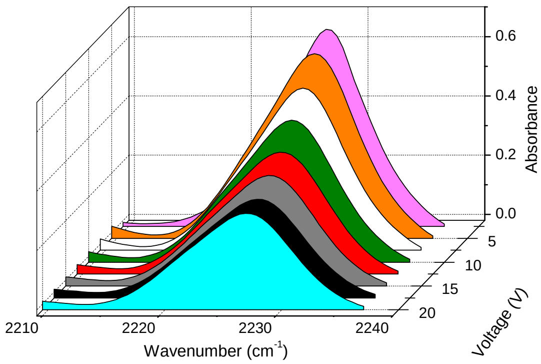


Fig. 4. Area of the C≡N stretching peak at 2226 cm^{-1} (2205-2250 cm^{-1}) versus applied voltage.

As also depicted in figure in figure 3, the electric field has a strong influence on the dichroic ratio in the range 2–20V, when R increases from 0.4 to 1.6. Higher than 20V, the variation is significantly smaller, meaning that the majority of the NLC molecules now have a general homeotropic allignment.

4. Conclusions

The study of the molecular layout of NLC molecules in various micro scale patterns is an important topic, not only for the directly involved physical arguments, but also for advancing the understanding of the complex physical processes and phenomena that govern nano and micro scale level interactions. In this paper we have characterized by means of a transmission microspectroscopic FTIR (Fourier Transform Infrared Spectroscopy) sampling technique, the orientational behavior of a nematic liquid crystal inside EHD generated polymeric microcavities. The initial radial alignment of the NLC molecules inside the cavities is no longer preserved when applying an external electrical field to our system. Following the experimental measurements, we determine the dichroic ratio for various applied voltage values when considering different absorbance peaks with suitable parallel and perpendicular polarization tendencies. At a threshold value of 20V most of the molecules inside the cavity can be considered as being reoriented parallel with the electric field. The results are in good agreement with other data from scientific literature and Monte Carlo simulations performed on similar materials [20,21]. These liquid crystalline systems are already extremely interesting from a theoretical point of view, but their true potential lies in the prospective technological and industrial applications.

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References

[1] B. R. Acharya, J-H. Kim, S. Kumar Phys. Rev. E **60**(6), (1999).
[2] A. L. Ionescu, A. Ionescu, E. S. Barna, V. Barna, N. Scaramuzza, Appl. Phys. Lett., **84**(1), 40 (2004).
[3] A. L. Ionescu, A. Ionescu, E. S. Barna, V. Barna, N. Scaramuzza, J. Phys. Chem.B **108**(26), 8894 (2004).
[4] V. Barna, S. Ferjani, G. Strangi, A. De Luca, C. Versace, N. Scaramazza, Appl. Phys. Lett. **87**, 221108 (2005).
[5] V. Barna, R. Caputo, A. De Luca, N. Scaramuzza, G. Strangi, C. Versace, C. Umeton, R. Bartolino, G. N. Price, Opt. Exp. **14**(7), 2695 (2006).
[6] N. Scaramuzza, C. Berlic, E. S. Barna, G. Strangi, V. Barna, A. Th. Ionescu, J. Phys. Chem. B **108**(10), 3207 (2004).
[7] S. Ferjani, V. Barna, A. De Luca, N. Scaramuzza, C. Versace, C. Umeton, R. Bartolino, G. Strangi, Applied Physics Letters **89**, 121109 (2006).
[8] B. Jerome, Y. R. Shen, Phys Rev E ,**48**, 6 (1993).
[9] S. D. Evans, H. Allinson, N. Boden, T. M. Flynn, J. R. Henderson, J. Phys. Chem. B **101**, 2143 (1997).
[10] W. M. Gibbons, P. J. Shannon, S.-T. Sun, B. J. Swetlin, Nature **351**, 49 (1991).
[11] G. Strangi, E. Cazzanelli, N. Scaramuzza, C. Versace, R. Bartolino, Phys. Rev. E. **62**, 2 (2000).
[12] V. Barna, A. De Luca, C. Rosenblatt, Nanotechnology **19**, 32 (2008).
[13] P. Chaudhari et al., Nature **411**, 56 (2001).
[14] V. Barna, A. De Luca, T. Atherton, G. Carbone, M. Sousa, C. Rosenblatt, Nature Physics, **4**, 869 (2008).
[15] P. G. de Gennes, The Physics of Liquid Crystals, Clarendon, Oxford (1974).
[16] S. Faetti, G. C. Mutinati, Phys. Rev. E. **68**, 026601 (2003).
[17] V. Barna, G. Strangi, E. S. Barna, J. Optoelectron. Adv. Mater. **10**(12), 3403 (2008).
[18] X. Nie, Y-H. Lin, T. X. Wu, H. Wang, Z. Ge, S-T. Wu, J. Appl. Phys., **98**, 013516 (2005).
[19] S. Chandrasekhar, Liquid Crystals, Cambridge University Press (1993).
[20] C. Berlic, V. Barna, J. Optoelectron. Adv. Mater. **12**, 1427 (2010).
[21] C. Berlic, V. Barna, Optics Express, **18**(23), 23646 (2010).
[22] E. Schäffer, T. Thurn-Albrecht, T. P. Russell, U. Steiner, Nature, **403**, 874 (2000).
[23] G. P. Crawford, S. Žumer, Liquid Crystals in Complex Geometries formed by polymer and porous networks, Taylor and Francis (1996).
[24] C. A. McFarland, J. L. Koenig, J. L. West, Appl. Spectrosc. **47**, 321 (1993).
[25] H. Binder, H. Schmiedel, G. Lantzsch, C. Cramer, G. Klose, Liq. Cryst., **21**, 415 (1996).
[26] T. I. Urano, H. Hamaguchi, Chem. Phys. Lett., **195**, 287 (1992).

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