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Raman mapping of Polymer Dispersed Liquid Crystal

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Abstract

The electro-optical properties of polymer dispersed liquid crystals (PDLC) materials make them interesting for display applications, especially as light modulators through a controllable scattering effect. Their electro-optical performances are strongly correlated with the distribution of the liquid crystal director inside the droplets. We showed that the Raman spectrometry mapping allows to evidence the director distribution of liquid crystal molecules in a confined geometry. In this study, we have focused our attention to the case of nematic liquid crystal (5CB) droplets dispersed in a polymer matrix (PMMA). Considering the characteristic C≡N polarized triple bond we have observed a change of the Raman spectrometry images by varying the orientation of the droplet axis versus to the pump beam polarization. To explain these changes, we purpose to use the classical bipolar droplet model. This ideal representation of the liquid crystal organisation inside the droplet enabled us to easily determine the general form of the Raman spectrometry maps.
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1. Introduction

Liquid crystals (LCs) spatially confined to curved geometries have been the subject of considerable experimental and theoretical research in the last few years [1], due to the nature of physical phenomena involved in these systems, such as changes on the nature of the phase transitions, the reduction of transition temperatures and changes of the LC director (i.e. the macroscopic orientation of the molecules)[2] configuration in small cavities. The majority of studies focus on the role played by the dimensionality and finite size effects on the physical properties of confined LCs. The explanation that is recognized as fundamental to describe the changes on these physical properties was the interplay between the ordering interactions at the surface of the cavity walls and the elastic deformation energies of the bulk LC. To achieve confining dimensionality and finite size effects in LCs, needs to confined it in thin films, porous glasses with controlled pore sizes, aerogels as well as in microdispersions form within a polymer matrix (so-called polymer dispersed liquid crystals (PDLCs))[1,3]. In the case of mixtures of polymer and liquid crystal, a macroscopic phase separation occurs, and a smectic [4] or nematic [5] liquid crystalline ordering was segregated within randomly dispersed micrometer sized droplets from the polymer rich phase. Theses composite materials offer considerable promise for large area flexible displays and switchable windows applications [5]. In PDLCs using a nematic phase as the dispersing LCs, the principle of the switching operation consists on the reorientation of the mean nematic director upon application of an electric field greater than a critical threshold. This reorients the director along the electric field, changing the effective refractive index of the LC droplets, reducing the scattered transmitted

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light and switching the device on. For an electric field smaller than the critical one the scattering of the transmitted light increases and the device is switched off. The relaxation dynamics of the LCs molecules and the switching mechanism between the on–off states depend on the original droplet nematic-director distribution [3,6]. Thus, to achieve a better understanding of these switching mechanisms, it is essential to determine unambiguously the director-field distribution in drops.

Among experimental methods, confocal polarized micro-Raman spectroscopy proves to be successful for molecular orientation analysis [7] and particularly for the studies of local properties of liquid crystals [8,9,10]. Raman scattering combines several advantages over other spectroscopic techniques, including the fact that it is noninvasive, it has remarkable spatial resolution (few micrometers); moreover, the confocality assures the three-dimensional analysis of a material.

In the present study we investigate, using confocal micro-Raman spectrometry a PDLC material and used this technique as an experimental tool to probe LC ordering and director-field distribution inside individual droplets. The PDLC material used in this work is based on a mixture of a thermoplastic polymer (polymethylmethacrylate: PMMA) and a low molecular weight nematic LC (pentylcyanobiphenyl: 5CB). The investigation of this composite system is favorable because it is made of only two molecular species, thus avoiding the complexities of the interpretation of Raman spectra inherent in multi-component systems.

2. Experiment

2.1. Preparation of the samples

PMMA of molecular weight of $M_w = 100 \times 10^3$ g/mol and 5CB were purchased from Aldrich and used without further purification. The phase sequence for bulk 5CB is crystal (K)–nematic (N)–isotropic (I), and the phase transitions upon slow heating from the crystalline phase occur at $T_{KN} = 23\,^\circ$C and $T_{NI} = 35.3\,^\circ$C. Blends of PMMA and 5CB were prepared by a combination of solvent induced and thermally induced phase separation processes. A mixture of PMMA and 5CB with LC concentration of 57 wt.% were dissolved in tetrahydrofuran at room temperature at 80 wt.%. The solution was stirred mechanically for 15 h. A small amount of the solution was then cast on carefully cleaned glass substrate, and the sample was left for 14 h to allow a complete evaporation of the solvent. Another glass substrate was put on the top of the first one, and the dry sample was sandwiched between the two glass substrates and pressed. During this procedure, the sample was kept at 100 °C for several hours, and then slowly cooled to room temperature to induce phase separation. It was then annealed at 27 °C for 12 h to promote coalescence of LC

droplets, leading to morphologies with separated drops of the average size of about 5–10 μm. Nevertheless, one thinks that the complete phase separation between the LC and the polymer was still not attained, and that a small fraction of the liquid crystal remains dissolved in the polymer [11]. The morphologies of PDLC samples were determined by means of polarizing optical microscope (POM) (LEICA DMRXP), with sample cells placed between crossed polarizers.

2.2. Raman scattering experiments

The Raman measurements were carried out with a Dilor XY-800 confocal micro-Raman spectrometer [12]. The spectra were recorded using the 514.5 nm line of an Ar/Kr ion laser. The PDLC sample was mounted on an automated xy translation stage (Jobin-Yvon Horiba) controlled by a computer. The data were collected at room temperature (20 °C). The mapping was obtained by focusing the laser beam with a 50 × magnification in the $Z\,(XX)\,[\bar{Z}]$ configuration.

3. Results and discussion

To probe the orientational order in 5CB droplets we have used the C≡N stretching vibrational band [9,13] at 2226 cm^{-1} (Fig. 1). This band is very interesting because the cyano-vibration is highly polarized and the direction of this vibration is, with a good approximation, parallel to the mean director direction. Thus, the Raman study of the C≡N stretching mode behaviour gives a useful tool to probe the distribution of the director. Moreover, as the Raman signal scattered by the C≡N bond is polarized: the intensity of the band associated to this vibration is maximal when the pump beam polarization is parallel to the director and is minimal when the polarization of the pump beam is perpendicular to the director. Hence, the polarized micro-Raman imaging of PDLC provides easily local informations on the molecular orientation inside the LC droplets.

3.1. Raman imaging of PDLC

We report below, the results obtained on a single 10 μm diameter LC droplet (Fig. 2).

The sample was put on a rotating stage (Newport-Model ESP100), and we define the angle θ between the droplet axis and the pump beam polarization direction $E_i \rightarrow$ (Fig. 2). The selected area was divided into 0.2 μm × 0.2 μm size pixels. We recorded the spectra in the range 2000–2500 cm^{-1} with a spatial resolution of 0.2 μm. All spectra were fitted with a Lorentz function and a linear baseline.

Concerning the confocal property of the microscope, we have used the formalism of Everall [14,15] which takes into account of distortion created by interface between two mediums. A simple calculation shows that this depth (over 50 μm) is larger than the droplet thickness (estimated