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The influence of single-walled carbon nanotubes on optical properties of the poly[(2,5-bisoctyloy)-1, 4-phenylenevinylene] evidenced by infrared spectroscopy and anti-Stokes photoluminescence

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ABSTRACT

Significant differences are reported for the IR spectra of poly[(2,5-bisoctyloy)-1, 4-phenylenevinylene] (BO-PPV) recorded onto the KBr, Ag and Au supports. In this work, a decrease in the absorbance of the IR spectra of the BO-PPV films deposited onto Au and Ag supports as increasing the macromolecular compound film thickness is reported. A preferential orientation of the BO-PPV molecules and its composite with single-walled carbon nanotubes (SWNTs) versus metallic supports of Ag and Au is assessed using the IR absorption spectroscopy under ***s*** and ***p*** polarized light. An anti-Stokes photoluminescence (ASPL) is reported to characterize the BO-PPV macromolecular compound. The BO-PPV ASPL spectra intensity dependent both of the thickness of the macromolecular compound layer deposited onto the metallic supports and the SWNTs weight in the BO-PPV/SWNTs composite mass.

1. Introduction

Much effort has been made over the past 20 year in the knowledge of the vibrational properties and the photoluminescence (PL) of the composites based on conjugated polymers (CPs) and carbon nanotubes (CNs) [1]. A part of this effort has been focalized on: i) the elucidation of the chemical interaction between the two constituents by resonant anti-Stokes and Stokes Raman scattering or surface enhanced Raman scattering (SERS), when was invoked either a covalently/non-covalently functionalization of CNs with CPs, either a doping process of CPs with the CNs anion radicals [1]; ii) the assessing of the role of metallic and semiconducting CNs both on the CPs PL quenching process [2] and photochemical processes [3]; iii) the understanding of the adsorption mechanism of composites onto metallic support by surface-enhanced infrared absorption spectroscopy (SEIRA) [2,4]. A large number of the CPs/CNs composites were studied by different researcher, some examples in this sense correspond to CNs functionalized with: i) polyaniline [5], ii) poly(*para*-phenylene vinylene) (PPV) [6], iii) poly(3, 4-ethylenedioxythiophene) [7], iv) polypyrrole [8], v) polyfluorene [9] and so on. Despite this effort, at present, little information are known about the composites based on singles-walled carbon nanotubes (SWNTs) and poly[(2,5-bisoctyloy)-1, 4-phenylenevinylene] (BO-PPV) [10]. According to Ref. [10], the main features of the BO-PPV/SWNTs composite known until now regard: i) the molecular structure of this composite corresponds to BO-PPV covalently functionalized SWNTs, as a result of the charge transfer between the two constituents which takes place by the mixing of SWNTs with BO-PPV; ii) the BO-PPV PL quenching is due to metallic tubes; and iii) the electrochemical doping of the BO-PPV/SWNTs composite induces steric hindrance effects as a result of the presence of anions which compensate the positive charges generated onto macromolecular chain. In the context of the progress reported for the PPV macromolecular compound, it is worth mentioning: i) the anti-Stokes photoluminescence (ASPL) of PPV and its composites with SWNTs [11] and ii) the assessing of the influence of the Au and Ag supports on the orientation of PPV macromolecular compound and the PPV/SWNTs composite obtained by the annealing conversion of the PPV precursor solution in absence and in the presence of different SWNTs weight percentages [12]. Compared to this progress, in the present work, a special attention will be given to: i) the highlighting of the dependence of the IR spectra with the BO-PPV films thickness deposited onto the rough Ag and Au

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supports; ii) the illustration of the influence of the SWNTs on the orientation of the BO-PPV molecules onto the two rough metallic supports; and iii) the dependence of the ASPL intensity of BO-PPV with the thickness of the macromolecular compound layer deposited onto the rough metallic supports and the ASPL quenching of BO-PPV in the presence of SWNTs.

2. Experimental

The compounds BO-PPV and $CHCl_3$ were purchased from Sigma-Aldrich, while SWNTs synthetized by a high-pressure CO disproportion (HIPCO) were bought from Nanointegris. In this work were prepared: i) the solutions of BO-PPV in $CHCl_3$ with the concentrations equal with 2 wt%, 1 wt% and 0.5 wt% and ii) the mixtures of BO-PPV and SWNTs in $CHCl_3$ with the weight ratios of 1:0.1 (labeled M_1) and 1:0.5 (labeled M_2) and 1:1 (labeled M_3), which were ultrasonically homogenized for 30 min, when composites of the type of BO-PPV covalently functionalized SWNTs (BO-PPV/SWNTs) were obtained [10]. The films of BO-PPV and BO-PPV/SWNTs with the thickness 25, 50 and 100 nm were deposited onto the rough Ag and Au supports prepared according to the protocol described in Ref. [13].

The IR spectrum of BO-PPV in transmission geometry was recorded using a Bruker FTIR spectrophotometer, Vertex 80 model. The IR spectra of BO-PPV and its composites with SWNTs in the grazing-incidence angle reflection geometry under ***p*** and ***s***-polarized light were recorded with the same equipment, which was endowed with a Hyperion 2000 FTIR microscope that has a grazing angle objective.

The ASPL spectra of BO-PPV and the BO-PPV/SWNTs composite were recorded under the excitation wavelength of 676.4 nm, at room temperature, using a Jobin-Yvon T64000 Raman spectrophotometer equipped with a Krypton laser from Spectra Physics.

3. Results and discussion

Fig. 1a shows IR spectrum of BO-PPV obtained by the KBr pellet method. The main absorption bands are situated at 698–724, 966, 1043–1066, 1202, 1254, 1352–1387, 1421–1468, 1506, 1600, 1610–1700 and 1739 cm^{-1}, they being assigned to the following

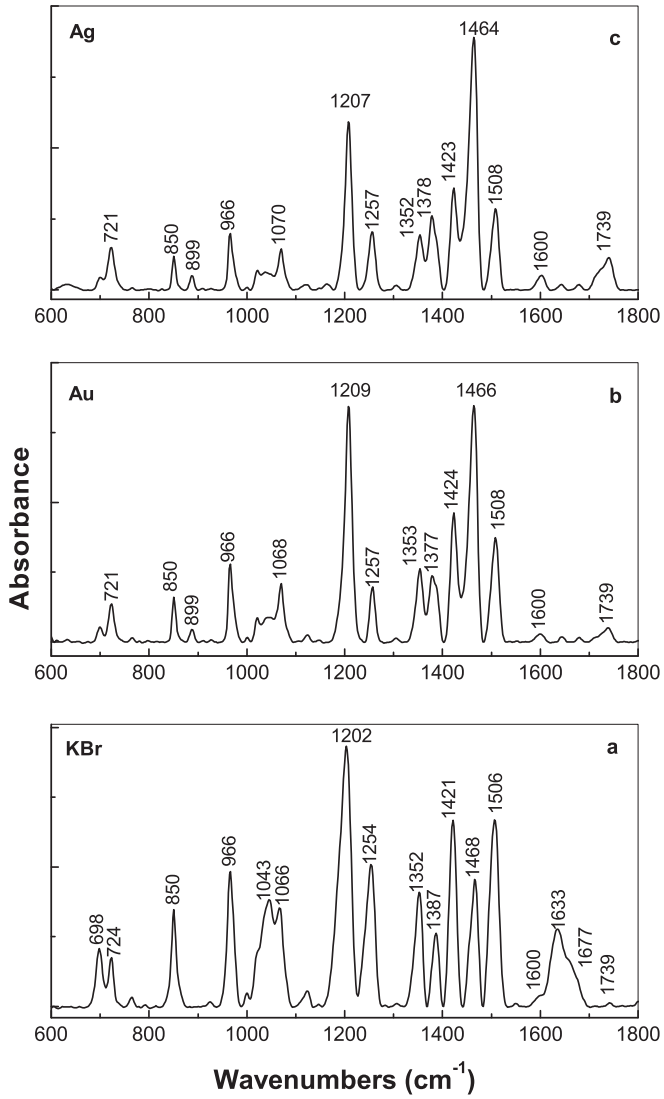

Fig. 1. IR spectrum of BO-PPV recorded using the KBr pellet method (**a**). IR spectra of the BO-PPV films deposited onto the rough metallic supports of Au (**b**) and Ag (**c**). The thickness of the BO-PPV films deposited onto the rough Au and Ag supports was of 50 nm.

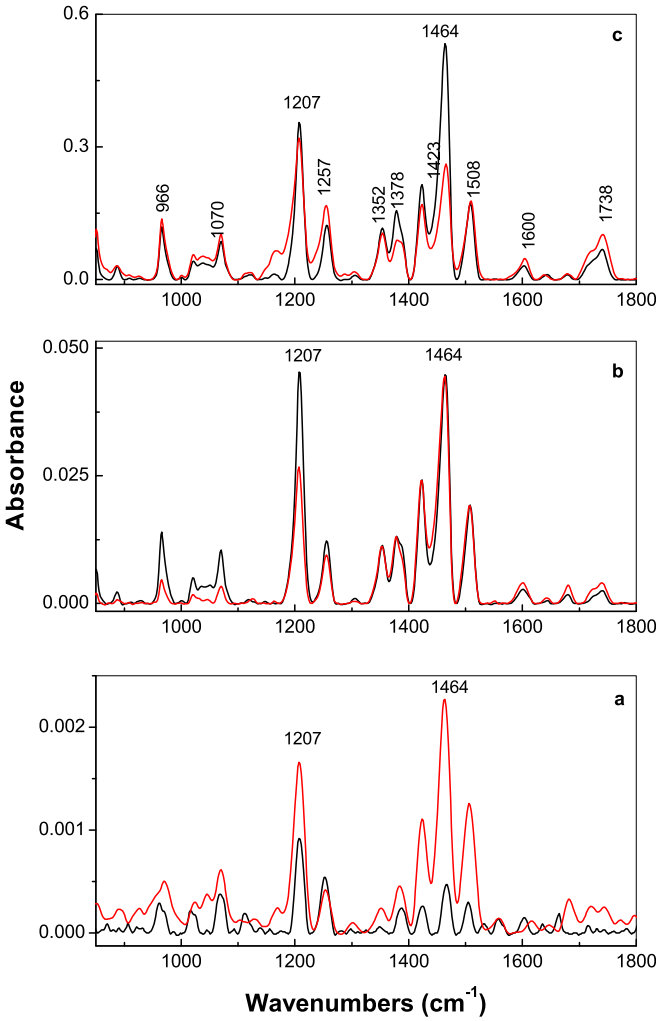

Fig. 2. IR spectra in the grazing angle incident reflection geometry, under ***p*** (black curves) and ***s*** (red curves) polarized light, of the BO-PPV films with the thickness of 25 (**a**), 50 (**b**) and 100 nm (**c**) deposited onto rough Ag supports. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)