



## Molecular structure of poly(3-alkyl-thiophenes) investigated by calorimetry and grazing incidence X-ray scattering

Jose Abad<sup>a,b,\*</sup>, Nieves Espinosa<sup>c</sup>, Pilar Ferrer<sup>e,f</sup>, Rafael García-Valverde<sup>c</sup>, Carmen Miguel<sup>c</sup>, Javier Padilla<sup>b</sup>, Alberto Alcolea<sup>d</sup>, German R. Castro<sup>e,f</sup>, Jaime Colchero<sup>a</sup>, Antonio Urbina<sup>c</sup>

<sup>a</sup> Departamento de Física, Centro de Investigación en Óptica y Nanofísica, Universidad de Murcia, Campus de Espinardo, 30100 Murcia, Spain

<sup>b</sup> Departamento de Física Aplicada, Universidad Politécnica de Cartagena, Plaza del Hospital 1, 30202 Cartagena, Spain

<sup>c</sup> Departamento de Electrónica, Universidad Politécnica de Cartagena, Plaza del Hospital 1, 30202 Cartagena, Spain

<sup>d</sup> Servicio de Apoyo a la Investigación Tecnológica (SAIT), Universidad Politécnica de Cartagena, Plaza del Hospital 1, 30202 Cartagena, Spain

<sup>e</sup> SpLine, Spanish CRG beamline at the ESRFacility, 6 rue Jules Horowitz B.P. 38043 Grenoble, France

<sup>f</sup> Instituto de Ciencia de Materiales de Madrid, CSIC, calle Sor Juana Inés de la Cruz, 3, 28049 Madrid, Spain

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### ABSTRACT

A study of the molecular structure of regio-regular bulk poly-3-octyl-thiophene (P3OT) and poly-3-hexyl-thiophene (P3HT) and the phase transitions during heating and cooling scans in a temperature range of  $-158$ – $773$  °C has been performed by means of calorimetry of bulk samples and grazing incidence X-ray diffraction from synchrotron radiation. Additional calorimetric measurements were performed on samples in toluene solution. From the calorimetric temperature diagrams at different scan rates, we obtain the melting and crystallization temperatures, and we identify a low temperature calorimetric glass transition. This transition is expected because of the coexistence of amorphous and crystalline phases, which is further supported by scanning force microscopy images where lamellar structures have been observed. Thin films of both polymers have also been studied by grazing incidence X-ray diffraction, and the evolution of the (1 0 0) crystalline peak monitored as a function of sample temperature, showing different behavior in both polymers, *d*-spacing increases in P3HT and decreases in P3OT for increasing temperatures. The information presented in this article will be useful to design fabrication techniques for organic-based electronic devices, which could include high and low temperature cycles combined with structural quenching procedures.

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### 1. Introduction

The semiconducting materials composed of  $\pi$ -conjugated polymers have been studied since long time ago [1], and more recently have attracted further attention due to their potential applications in optoelectronic devices such as organic solar cells [2–4], thin film transistors [5] and light-emitting diodes [6,7]. A huge research effort has been devoted to understand the correlation between their structural properties and their performance as active layers in organic electronic devices. More recently, the development of the bulk heterojunction approach in organic light emitting diodes (OLEDs) and solar cells (OSCs) has created great expectations: a rising organic optoelectronic industry could benefit from highly efficient routine roll-to-roll packaging technologies [8,9] that can be combined with ink-jet or printing procedures

[10,11]. Numerous film forming techniques have been explored and the ideal process seems to involve solution processing of the organic layers to provide a less energy intensive manufacturing. The application of roll-to-roll techniques using liquid-state coating and printing methods with no vacuum, has been demonstrated recently on a preindustrial scale [8]. These techniques could yield a huge low cost throughput provided that the structural and dynamical properties of these polymers are understood and a controlled self-organization process at the nanoscale is developed.

The best devices so far have been constructed using the “bulk heterojunction” concept, where a blend of two materials is prepared to create a distributed *p*–*n* junction: one acts as an electron donor, the other as an electron acceptor. The two percolative networks created in the blend should mix in a nanometer scale fitted to the mean free path of the exciton formed by light absorption. The conjugated polymers, and particularly some functionalized polythiophenes, have been the materials most used as electron donors, and therefore acting as hole conductors or *p*-type materials. It has been observed that the performance of the devices is strongly dependent on thermal

\* Corresponding author at: Departamento de Física Aplicada, Universidad Politécnica de Cartagena, Plaza del Hospital 1, 30202 Cartagena, Spain.

Tel.: +34 868 07 1096; fax: +34 968 32 5337.

E-mail address: jose.abad@upct.es (J. Abad).

post-processing and blend composition. It has been showed that different thermal processes can increase the efficiency of the devices, but there is not a general agreement about the best thermal process. Furthermore, reasons for this efficiency increase are still unclear. Additionally, the choice for an optimum composition of the blends has risen some controversy [12]. A deep understanding of the dynamics of the pure components of the blend will help to optimize and control the processing of the mixtures. More recently, the synthesis of block copolymers, by adding blocks of non active structural polymers to blocks of the conventional photoactive polymers such as the poly-thiophenes has opened a new route towards the tailoring of dynamical and structural properties in order to control the nanostructure and therefore the performance of the final devices [13,14].

Thin films of poly-3-hexyl-thiophene (P3HT) and poly-3-octyl-thiophene (P3OT) have been previously characterized by scanning force microscopy and they show a layered structure where crystalline lamellar phases coexist with amorphous domains [15,16]. We have also performed previous X-ray diffraction experiments on P3OT samples and all of the spectra indicate the simultaneous presence of both crystalline and amorphous component as evidenced by sharp Bragg peaks and diffuse scattering, respectively [15]. In this article we will present a detailed calorimetric study of bulk samples of P3OT and P3HT and the results of grazing incidence X-ray scattering from synchrotron radiation on thin films of the same polymers spin-casted on different substrates. Additional calorimetric information of the polymers in toluene solution is also presented because the thin films have been processed from solution. The calorimetric scans performed at different temperature rates have allowed us to identify the melting and crystallization temperatures of bulk samples, giving evidence of a low temperature glass transition and indicating a constant ratio of crystalline to amorphous phases independent of annealing cycles or temperature scan rates. The calorimetric data on solution samples present enthalpy values for the low temperature crystallization of the solvent, which depend on the concentration of the polymers in solution, which ranges from 1% to 7%, covering all usual concentrations for device preparation from solution.

## 2. Experimental

Two regio-regular poly-alkyl-thiophenes, P3HT and P3OT, were studied by scanning calorimetric techniques and grazing incidence X-ray scattering. Both polymers were purchased from Sigma-Aldrich. They are regio-regular head-to-tail (more than 98.5%) with an average molecular weight around 25,000 for P3OT and 45,000 for P3HT and a 99.995% of purity, and polydispersity between 1.5 and 2. For scanning force microscopy (SFM) and GIXRD measurements P3OT and P3HT samples were prepared by spin-coating. A solution of 20 mg/ml P3OT (9 mg/ml, P3HT) in toluene was prepared, a 10  $\mu$ l drop of this solution was deposited on a glass cover slip and then accelerated to about 3000 rpm. During this process, the drop is homogeneously spread out and a thin film P3OT (P3HT) sample is formed on the substrate. For calorimetric measurements, the bulk polymers were weighed in a microbalance and encapsulated in an aluminum capsule (keeping constant pressure by means of a small hole in the capsule). For the solution calorimetric studies, different solutions ranging from 1% to 7% were prepared for both polymers using toluene as solvent, in this case, the aluminum capsule was sealed and the scans only reached 25 °C avoiding pressure building up within the capsule. Differential scanning calorimetry (DSC) was performed at different temperature scan rates using a Mettler-Toledo DSC822e calorimeter. Nitrogen was used as purge gas, and samples were

scanned at 1, 6, 10, 15, 20, 25 and 30 °C min<sup>-1</sup> in a temperature range spanning from -145 °C to 250 °C. The amount of sample used was 10.18 mg for P3HT and 10.01 mg for P3OT allowing us to keep the heat flow needed to conduct the experiments in the range of 0.5–15 mJ s<sup>-1</sup>, matching the optimum range of the instrument. For all the solutions a total mass around 12 mg was used. These mass values were also used to obtain an estimated heat capacity at constant pressure from our heat flow measurements for both materials. Scans of an empty aluminum container were taken in order to obtain a data file that allowed us to perform background correction.

The morphology of the thin films was studied at room temperature and ambient conditions using SFM. A Nanotec Electronica SFM system with a phase locked loop (PLL)/dynamic measurement board was used with Olympus OMCL-AC-type cantilevers (nominal force constant: 2 N/m; resonance frequency: 70 kHz). Unless specified otherwise, imaging was performed in non-contact dynamic SFM (NC-DSFM) using the oscillation amplitude as feedback parameter, for more information see [16].

GIXRD is a very suitable technique to track the eventual structural changes with an information depth selected at will from few unit cells to several hundreds of microns by changing the incidence angle. We therefore used GIXRD to characterize the polymer layers orientations. The GIXRD experiments were carried out at fixed wavelength of 0.826 Å on a six-circle diffractometer at SpLine beamline (BM25B), European Synchrotron Radiation Facility (ESRF), Grenoble, France [17]. A point scintillation detector, which allows performing high-resolution diffraction experiments, was used. The sample was placed on a heating stage covered with an air-tight Kapton housing filled with 1 bar of nitrogen in order to avoid the degradation of the sample. Two incidence angles,  $\alpha=0.15^\circ$  and  $2.00^\circ$ , have been used and the temperature range was from 21 °C to 120 °C.

## 3. Results and discussion

It is generally accepted that polyalkylthiophenes are semi-crystalline with crystalline domains surrounded by amorphous material. The crystalline domains have a orthorhombic unit cell (see Fig. 1) with lattice parameters in case of P3OT  $a=2.07$  nm,  $b=0.76$  nm and  $c=0.77$  nm and for P3HT  $a=1.68$  nm,  $b=0.76$  nm and  $c=0.77$  nm [18,19]; where – following the usual convention – the lattice parameter  $a$  is along the direction of the alkyl tails of the molecule, the parameter  $b$  along the stacking direction of the molecules (perpendicular to the projection shown in Fig. 1) and the direction  $c$  is along the backbone of the molecule.

We present the measurement results in different subsections, the first one devoted to the morphology of the films, the second one will present calorimetric measurements performed on both bulk polymers (P3OT and P3HT) and its toluene solutions, and the third one will show the GIXRD results.

### 3.1. Morphology

Fig. 2 shows topography images (a) and (b) of a P3OT thin film and (c) and (d) of a P3HT thin film prepared using an equivalent protocol. In the morphology of the P3OT thin films (a) and (b) two distinct regions are clearly distinguished: a lower region, which usually covers most of the sample, and a second higher region with a characteristic layered structure. A detailed study about the morphology of the P3OT thin films is found in reference [20]. The structures corresponding to the higher regions have one or two layers, even though occasionally up to 5 layers have been observed and each layer has a height around 4–5 nm. This corresponds to the double of  $a$  lattice parameter of crystalline

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