



Poly[(9,9-dioctylfluorene)-2,7-diyl-alt-(4,7-bis(3-hexylthien-5-yl)-2,1,3-benzothiadiazole)-2',2''-diyl]:PCBM thin films: Molecular self-assembly, hexyl substituent groups and sheet resistance relationships

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ABSTRACT

Poly[(9,9-dioctylfluorene)-2,7-diyl-alt-(4,7-bis(3-hexylthien-5-yl)-2,1,3-benzothiadiazole)-2',2''-diyl] (F8TBT) is a conjugated polymer with peculiar characteristics due to its D-A type architecture. F8TBT ambipolar feature has allowed the confection of F8TBT/PCBM ([6,6]-Phenyl-C₆₁-butyric acid methyl ester) and polymer/F8TBT heterojunctions for solar cells. However, the use of PCBM as electron acceptor in photovoltaic devices is still sovereign because of its great electron affinity and compatibility with a large amount of conjugated polymers.

The effects of PCBM content (0, 33, 50, 67, 75 and 80 wt%) and amount of hexyl substituent groups in F8TBT polymer backbone on morphology and Hall sheet resistance (R_s) of F8TBT:PCBM thin films are evaluated quantitatively by optical microscopy and image processing. Circular-like cavities are formed on F8TBT films by molecular self-assembly, such structures on F8TBT film surface were identified by AFM. The statistical distributions of the self-assembled cavity diameters can be fitted by Lorentz, Boltzmann sigmoidal and Gauss statistics functions, depending on the amount of hexyl substituent groups and PCBM. The absence of these alkyl groups on the polymer chains causes the following effects: increasing of the R_s value on 69% and modification of the cavity size distribution. Moreover, there is significant elevation of R_s due to the cavity density on polymer and nanocomposite thin films.

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1. Introduction

Conjugated polymers are great candidates for replacing the silicon technologies in electronic and optoelectronic applications due to their advantages over these non-organic materials, such as low manufacturing cost, light-weight and flexible displays, as well as greatest design freedom and shortest producing time of gadgets [1,2,3–4]. However, electronic devices containing conjugated polymeric systems have problems to achieve efficiency and living time comparable to those based on inorganic semiconductors.

These polymers are macromolecules with a peculiar chemical structure, which has alternating single and double chemical bonds that leads to a delocalization of electrons in the π -bonds (π -electrons) [5]. The semiconducting properties of conjugated copolymers are related to the π -electron density delocalization

along the macromolecules, but the π -bonds conjugation can be present in the polymer chain, in side groups linked to the polymer chain, or confined in segments in the polymer backbone [6,7].

Poly[(9,9-dioctylfluorene)-2,7-diyl-alt-(4,7-bis(3-hexylthien-5-yl)-2,1,3-benzothiadiazole)-2',2''-diyl] (F8TBT) is a conjugated copolymer with architecture like donor-acceptor electron type (D-A), which is a polymeric system that can improve the efficiency of polymer photovoltaic devices (PPVs) due to a better overlap between the solar emission and polymer absorption spectra [8,9]. This phenomenon occurs because of the alternating combination of electron donor (D) and electron acceptor (A) units on polymer chain allows the designing of low bandgap polymers. Since, the bandgap of the copolymer is determined by the combination of HOMO and LUMO levels from donor and acceptor units on polymer backbone, respectively [10–12]

Supramolecular self-assembly is a process in which molecules and macromolecules, such as polymeric chains, spontaneously form aggregates that leads to formation of organized structures

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with different size scales [13] Polymer self-assembling is caused by intra- and intermolecular interactions between polymer chains, being van der Waals forces, hydrogen bonds, electrostatic interactions, hydrophobic and hydrophilic effects, and π - π stacking those interactions [14] Self-assembled structures are commonly found in block copolymers [15–17], but non-block conjugated copolymers can suffer self-assembling process depending on the chemical structure, solvent polarity and room temperature [18]. In this regard, the achievement of self-assembled geometries in conjugated polymers has been a new way to modify the functions and physical properties of conjugated polymeric systems, which can be interesting to sensor and bioimaging applications [19].

F8TBT has been applied successfully on polymer light-emitting diodes [20–22], polymer/polymer solar cells [23,24], polymer/fullerene solar cells [25–28]. In PPV architectures based on F8TBT, it is mainly used [6,6]-Phenyl-C₆₁-butyric acid methyl ester (PCBM) as electron acceptor phase, which is a functionalized fullerene molecule with suitable solubility and good compatibility for the most conjugated polymers used as active layer on PPVs [29]. For the development of this nanostructured electronic, it is undeniable the importance of atomic force microscopy (AFM) for the identification of self-assembled structures and morphology characterization of the PPV active layers based on bulk hetero-junctions films [30–33], but the use of other microscopies for this analysis is still scarce.

In this contribution, it has been proposed the usage of optical microscopy and image processing to investigate the correlation between self-assembled morphology and Hall sheet resistance of F8TBT:PCBM thin films, as well as how the hexyl substituent content on F8TBT affects this electrical propriety. They are topics that have not yet been reported by the scientific community.

2. Experimental

2.1. Materials

Chloroform (spectrophotometric grade), [6,6]-Phenyl-C₆₁-butyric acid methyl ester (>99%) and glass microscopy slides were obtained from Tedia, Aldrich and Precision Glass Line, respectively. The chemicals were used as received.

2.2. Polymers synthesis

Poly[(9,9-dioctylfluorene)-2,7-diyl-alt-(4,7-bis(3-hexylthien-5-yl)-2,1,3-benzothiadiazole)-2',2''-diyl] (F8TBT), poly[(9,9-dioctylfluorene)-2,7-diyl-alt-(4,7-bis(thien-5-yl)-2,1,3-benzothiadiazole)2',2''-diyl] (F8TBTa) and poly[(9,9-dioctylfluorene)-2,7-diyl-alt-[(4,7-bis(3-hexylthien-5-yl)-2,1,3-benzothiadiazole)-ran-(4,7-bis(thien-5-yl)-2,1,3-benzothiadiazole)]-2',2''-diyl] (F8TBTb) were synthesized and chemically characterized in previous work [34]. Fig. 1 shows the chemical structures of the synthesized copolymers. The difference between these polymeric materials is the

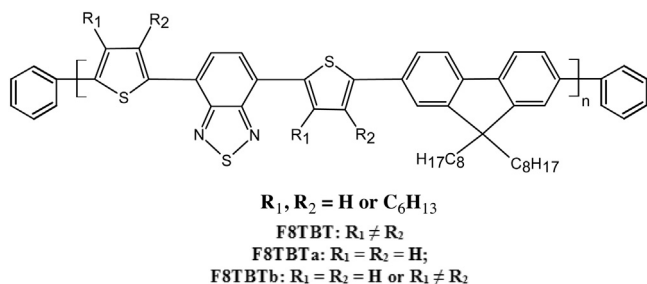


Fig. 1. Chemical structure of F8TBT, F8TBTa and F8TBTb copolymers.

content of thiophene ring with hexyl substituent groups: 0, 50 and 100% for F8TBTa ($M_w = 71,048 \text{ gmol}^{-1}$; PDI = 2.3), F8TBTb ($M_w = 12,204 \text{ gmol}^{-1}$; PDI = 1.8) and F8TBT ($M_w = 14,816 \text{ gmol}^{-1}$; PDI = 1.8), respectively.

2.3. Thin film preparation

The glass slides were pre-cleaned in acetone and ultrasonic bath for 20 min. Then the polymer:PCBM blends were deposited on the cleaned glass substrate by spin-coating (Swin 4 "Table Top Economic Coater, EC4 SYN 3S102-0902 model), 1900 rpm for 40 s, using solutions in spectral grade chloroform (2–8 mg/mL). Subsequently, the thin films were dried at 50 °C in a vacuum oven by 1 h.

2.4. Thin films characterizations

The surface morphology of the thin films was evaluated by optical microscopy on Olympus BX51 M optical microscope using reflectance mode. The surface optical micrographs were analyzed by ImageJ software. The sheet resistance (R_s) measurements were performed on Swin Hall 880 equipment by van der Pauw method. These electrical measurements were made in triplicate and, in this report, it is only introduced the arithmetical average of those R_s measures. The surface morphology of F8TBT thin film was characterized by atomic force microscope (AFM) in tapping mode with ScanAsyst method of the Multimode 8 probe microscope (Bruker).

3. Results and discussion

3.1. Thin film morphology

The surface micrograph of F8TBT thin film is shown in Fig. 2a, this film exhibits holes with several sizes on micrometer range, but there is indicative of cavities with dimensions at the nanometer scale. These circular structures were confirmed by AFM scanning (Fig. 3) and the F8TBT film thickness is $145 \pm 10 \text{ nm}$.

Mukherjee et al. [35] reviewed the literature about self-organization process. According to these authors, the morphology formation of circular-like patterns on polymer thin films, which have thickness less than 100 nm, is caused by spontaneous thin film rupture due to the intermolecular forces acting on polymeric film during deposition proceeding. As a consequence, the circular orifices are slowly generated on the polymer film and, in sequence, they grow exponentially (second stage) due to the coalescence of the cavity brims.

In contrast, Hemavathi and colleagues [36] have identified by AFM the same circular-like cavities on thin films of D-A conjugated copolymers with 3-cyanopyridine and arylene as acceptor and donor electron units, respectively. The formation of the circular orifices on film surface was attributed to supramolecular aggregates that were generated by self-assembling of copolymer chains.

Self-assembly feature of F8TBT has not yet been reported in the literature, but it is known that conjugated polymers with thiophene units have high intermolecular π - π stacking interaction, which induces self-assembling of polymer chains in solution and in solid state [37,38]. Specifically for thiophene-benzothiadiazole-thiophene segments (TBT) in F8TBT polymer backbone, the coplanarity and great π -conjugation of TBT frames may favor strong π - π stacking interactions, leading to aggregation and packaging of F8TBT polymer chains in solid state. Although ordered polymer structures by supramolecular organization can improve the transport of charge carriers of conjugated polymer thin films due to strong interaction between π -bonds [39], the formation of

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