

## Research paper

# Comparative analysis of contact resistance and photoresponse in poly(3-hexylthiophene) and poly(3-octylthiophene) based organic field-effect transistors



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## ABSTRACT

This paper explicitly explores the possibility of tailoring the performance of organic field-effect transistors (OFETs) fabricated using Poly(3-hexylthiophene) (P3HT) and Poly(3-octylthiophene) (P3OT) having different length of alkyl side chain. We observed that the performance of devices fabricated using P3HT were significantly better in comparison to that fabricated with P3OT. The estimated values of performance parameters of P3HT OFET were found to be significantly superior to those of P3OT OFET. Further, an order of magnitude lower contact resistance and higher photoresponse values were evident in P3HT OFETs. Moreover, the gate voltage tunability of photoresponse was also found to be significantly higher in P3HT OFETs highlighting its suitability over P3OT OFETs for photosensitive transistor applications. The results suggest that the alkyl side chain in Poly(3-alkylthiophene)s (P3ATs) is critical for achieving the optimized device performance and can be tailored in order to improve the performance of OFETs.

## 1. Introduction

Poly(3-alkylthiophene) (P3ATs) based solution processed organic electronic devices have been extensively investigated in past in order to utilize their unique features like mechanical flexibility, low fabrication cost and large area coverage [1–3] which are highly suitable for mass production of the consumer electronic products viz. large area displays, RF-ID tags etc. The performance of devices, utilizing P3ATs as active layers, such as organic solar cells (OSCs), organic light-emitting diodes (OLEDs) and organic field-effect transistors (OFETs) have been observed to be critically dependent on the charge transport properties of P3ATs which in turn is highly influenced by the overall morphology of the thin films consisting of P3ATs. In the past several groups have attempted to improve the overall morphology of conducting polymer thin films by incorporating various techniques viz. dip coating, drop casting, floating film transfer method, utilizing conducting polymers (CPs) having liquid crystalline properties etc. In this work we focus on the study of P3AT thin film based devices. In particular P3ATs having two different alkyl chains (hexyl and octyl) attached to the polymer backbone have been considered for the purpose of investigations. The variation in the alkyl side chain groups attached to the polymer backbone of P3ATs were found to influence bulk and interfacial thin film

morphology in OFETs based on them. Among some conventional organic electronic devices, OFETs find applications in the manufacturing of security tags, smart cards, flat panel displays and memories [4–6] apart from some other interdisciplinary applications like chemical/bio sensor, light-emitting devices and photosensors [7,8]. The morphology of P3AT films are significantly influenced by factors such as the regioregularity of polymer, thin film deposition technique, annealing temperature, boiling point of organic solvents etc. Apart from these the length of alkyl side chain in P3ATs, responsible for their solubility in organic solvents, severely affects the charge transport properties of thin films and ultimately the overall performance of based devices [9–12]. Thus, the optimization from the viewpoint of achieving reasonable solubility and at the same time ensuring remarkable charge transport properties of thin films is highly desired to make the fabrication process of polymeric solution processed devices and circuits more efficient.

The performance of P3AT based optoelectronic devices are severely affected by factors such as the extent of  $\pi$ -conjugation and disorder present in the polymer thin films [13,14]. Especially, in OFETs these parameters directly correlate with the field-effect mobility, current on/off ratio and contact resistance of the devices. Several reports can be found in literature that have systematically investigated and correlated the variation of these parameters to the performance of OFETs and

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several other electronic devices [15–24]. Although the performance of P3AT based OFETs have been studied appreciably well in past with the aim of exploring the dependency of different transistor performance parameters over the length of alkyl side chain [25]. In this article we have systematically investigated the variations induced by different lengths alkyl side chain in P3HT and P3OT based OFETs mainly in terms of their contact resistance and photoresponse values. Additionally, we analyzed and compared the possibility of gate voltage tunability of photosensitivity and responsivity values with respect to two different lengths of alkyl side chain.

## 2. Experiment

For comparative study with respect to change in the alkyl chain length, we have considered P3HT and P3OT based devices, we first ensured that the values of all other parameters such as regioregularity, molecular weight and polydispersity index of used polymers were well within the range so as to produce insignificant variations in the performance of devices. Since, it is well established that the regioregularity and the length of the alkyl side chain attached to polymer backbone influence the overall morphology as well as optical and electrical properties of the polymer thin films. The regioregularity values of polymers were estimated by  $^1\text{H}$  NMR (proton-nuclear magnetic resonance) spectroscopy. Fig. 1(a) and (b) represents the  $^1\text{H}$  NMR spectra of P3HT and P3OT recorded by Bruker AVANCE III-400 NMR machine at 400 MHz. The spectrum was individually recorded for the polymers dissolved in  $\text{CDCl}_3$ . The obtained spectra were used to calculate the extent of head-to-tail (HT) regioregularity values of used polymers. Mathematically, the regioregularity values were determined by the ratio of the peak's area at positions 2.8 ppm head-tail (HT) and 2.6 ppm head-head (HH) i.e.  $[\text{HT}/(\text{HT} + \text{HH})]$ . The estimated value of regioregularity of P3HT and P3OT was observed to be 98% each (insets of Fig. 1) [26,27]. The values of molecular weight and polydispersity index of P3HT were 54 kDa and 1.7 respectively whereas for P3OT the values were 25 kDa and 1.43 respectively. These values of molecular weight and polydispersity index are not expected to produce any significant amount of difference in the performance of P3HT and P3OT based OFETs [28–30]. This was also evident from the results in our earlier report, where it was explicitly showed that the polymer morphology changes when deposited over different surfaces in a single step (same regioregularity, molecular weight and polydispersity index) and this change was more prominent in P3OT [18].

Firstly, P3HT and P3OT thin films were prepared on glass substrates for the purpose of non-contact mode characterizations viz. absorption (UV–vis), photoluminescence (PL), Raman spectroscopy and X-ray diffraction (XRD). For this purpose glass substrates of size  $1\text{ cm} \times 2\text{ cm}$  were sequentially cleaned using ultrasonication in acetone and isopropanol for 10 min each. Next, a 0.5 wt% solution of regioregular Poly(3-hexylthiophene-2,5-diyl) (P3HT) and Poly(3-octylthiophene-2,5-diyl) (P3OT) (both used as purchased from Sigma Aldrich Co.) prepared

in anhydrous Chloroform were spin coated over the cleaned and dried substrates at 1500 r.p.m for 20 s. Subsequently, the thin films were annealed at  $90^\circ\text{C}$  for 2 h inside the  $\text{N}_2$  filled glovebox and allowed to cool down overnight prior to the characterization. The thicknesses of prepared P3HT and P3OT thin films were measured to be 48 nm and 45 nm respectively using VEECO optical profilometer. The UV–vis spectra were recorded by Agilent Carry 60 UV–vis spectrophotometer and PL spectra by FluoroMax-4p Spectrofluorometer from Horiba Jobin Yvon (Model: FM-100) with excitation and emission slit widths being set at 3 nm each and the samples were excited at 530 nm. X-ray diffraction (XRD) spectra of polymer thin films were recorded using a Rigaku Smart Lab system (with  $\text{Cu K}\alpha$  radiation at 40 kV and 40 mA with wavelength  $\lambda = 1.5418\text{ \AA}$ ). Raman measurements were carried out using LABRAM HR dispersive spectrometer equipped with a 632.8 nm excitation laser source of power 9 mW, an 1800 g/mm grating,  $100\times$  objective lens and a CCD detector.

Secondly, OFETs were fabricated in bottom gate bottom contact configuration. For this  $\text{SiO}_2(200\text{ nm})/\text{Si}$  substrates of size  $1\text{ cm} \times 2\text{ cm}$  were cleaned with the same procedure and the cleaned substrates were treated with Hexamethyldisilazane (HMDS) to make the surface of  $\text{SiO}_2$  hydrophobic. Gold electrodes of thickness 50 nm were deposited through a shadow mask having several channel lengths ( $L$ ) viz. 50, 75, 100, 150 and 200  $\mu\text{m}$  and width ( $W$ ) as 2 mm using the Physical Vapor Deposition system. The same solutions of P3HT and P3OT were then spin coated over the prepared substrates to fabricate the typical bottom gate bottom contact OFETs. The samples were finally annealed inside the  $\text{N}_2$  filled glovebox for the same duration and were also kept overnight prior electrical characterization using the Keithley 2612B sourcemeter. The schematic illustration of the fabricated OFETs is shown in Fig. 2. It must be noted here that the whole fabrication to electrical characterization process was performed inside the glovebox (under inert  $\text{N}_2$  atmosphere) system to rule any possibility of significant amount of unintentional doping. Also, the fabricated devices were annealed under inert environment for sufficiently long duration to completely remove the interstitially trapped solvent residues. Moreover the observed positive threshold voltages for OFETs fabricated using both P3HT and P3OT also points out to the fact that these OFETs are normally on, which can be attributed to the interface trap density or the conductivity of these thin films.

## 3. Results and discussion

### 3.1. Studies on morphological differences between P3HT and P3OT thin films

The morphology (grain size) of polymer thin films is very critical for improving the performance of organic devices. Particularly, in OFETs, where the charge transport occurs through narrow interfaces, the morphology of polymeric active layer becomes a major factor for optimizing the device performance. Hence, it would be interesting and

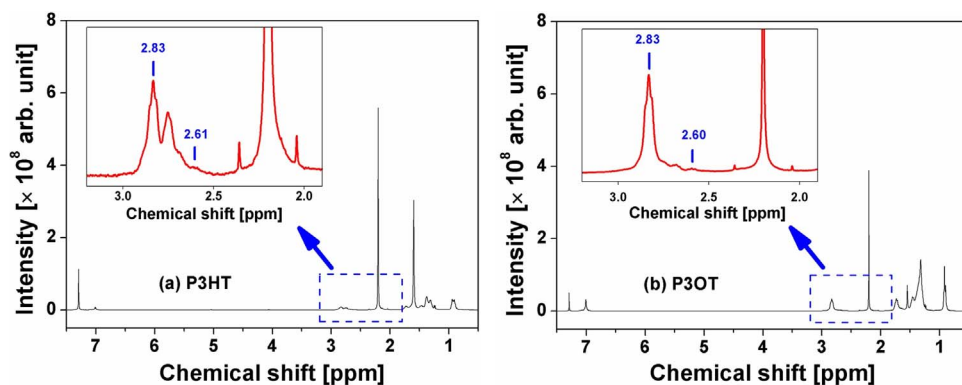


Fig. 1.  $^1\text{H}$  NMR spectra of P3HT and P3OT samples.

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