



Self-assembly of regioregular poly (3,3''-didodecylquarterthiophene) in chloroform and study of its junction properties



Manish Kumar Singh, Ashish Kumar, Rajiv Prakash *

School of Materials Science and Technology, Indian Institute of Technology, Banaras Hindu University, Varanasi 221005, India

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ABSTRACT

This article deals with the study of self-assembly of regioregular poly (3,3''-didodecylquarterthiophene), rr-PQT-12 into fiber form in chloroform by ageing process. Time dependent fiber growth mechanism is monitored by UV–vis absorption and confirmed by atomic force microscopy technique. It is observed that isolated rr-PQT-12 undergoes self-assembled fibril growth along π - π interaction direction and 45 min is sufficient for such assemblies in case of 0.125% w/v of rr-PQT-12 polymer in chloroform. Further the self-assembled fibril polymer is used in fabrication of Schottky diode. It exhibits ten times enhancement in forward current density (with one-fold higher mobility) and high rectification ratio compared to the isolated rr-PQT-12 due to the segmental electronic traps filling within stacking region. Our study provides a facile method of ordering of PQT-12 isolated chains in chloroform solvent and an effective way for improvement of performance of organic polymers based devices through such self-assembly.

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1. Introduction

Heterocyclic conducting polymers with mesoscale crystallization ability have been studied extensively in electronic devices due to high charge mobility in their self-ordered form [1–4]. Regioregular poly (3-hexylthiophene) (rr-P3HT) has considered as prominent material to fulfill these criteria [4–6]. Apart from rr-P3HT, poly (3,3''-didodecylquarter thiophene) (rr-PQT-12) has been also widely used alone or its composite form as active material in various applications like FET, diodes, sensors, solar cells etc. [5–11]. It is now well known that one of the crucial factors for charge carrier mobility in organic polymers is crystallinity and chain orientation in a successive fashion (collectively called ordered orientations) [12,13] so that carriers can hop through well connected crystalline regions. These types of orientations occur only if coiled unimers adopt an extended conformation by possible orientation in preferable conditions [5,6]. For example, due to rigid thiophene backbone, that facilitates π - π intermolecular interaction predominantly in one dimension like rr-P3HT which favors better electrical properties [11,14]. That is why the self-assembly of this polymer may give a breakthrough methodology for the enhancement in the properties of materials particularly for electronic applications [5,11–13]. Apart from this, self-assembled semiconducting polymers have segmental electronic traps within the

stacks of polymer chain, results the favorable charge transport by hopping or band transport [14–18]. Enormous efforts like ageing, ultra-sonication, thermal annealing, pressure dependent assembly solution, aggregation on lyophilic solvent surfaces (floating film transfer method) and vaporization technique have been applied for the ordering of the semiconducting polymers mainly P3HT [15–24]. Beside this, some other controlled techniques have also been applied for the ordering of several polymers which is liable to better charge transfer properties [25–27].

However, there is no report available on time dependent aggregation of rr-PQT-12 in marginal solvent at room temperature and its usage as an active material in diode fabrication at optimal conditions. In this paper, we report solvent driven optimization of fibril growth of rr-PQT-12 in chloroform and its charge transfer properties by fabricating sandwiched structure device (Schottky diode) compared to that of its isolated analogue (un-aggregated rr-PQT-12).

2. Experimental

2.1. Materials

rr-PQT-12 (ADS12PQT, Lot#14K007B1, molecular weight = 15,000–50,000 & HOMO = 5.24 eV & LUMO = 2.97 eV) was purchased from American Dye Source, Inc. USA and chloroform (analytical grade) was purchased from Merck, India.

* Corresponding author.

E-mail address: rprakash.mst@iitbhu.ac.in (R. Prakash).

2.2. Preparation of PQT-12 fibers

For the optimization of fiber formation, 0.125%, 0.055% and 0.026% w/v rr-PQT-12 solutions were chosen for the study. In this process, a stock solution of 0.5% w/v rr-PQT-12 was prepared with chloroform in sealed glass vials and completely dissolved by heating at 80 °C (optimum temperature). After complete dissolution, 250 μ L of this stock solution was further diluted by 750 μ L chloroform for the preparation of 0.125% w/v rr-PQT-12 and allowed to spontaneous cooling for 10 min to reach temperature in the range of 25°–27 °C in a closed chamber equipped with temperature controller. This particular solution was referred as 'isolated rr-PQT-12' throughout the experimentation. After that, this solution was kept 45 min to insure fiber formation which was further justified by UV–visible absorption study (Fig. 1 (II)). As the time passed, the color of rr-PQT-12 solution changed from light orange to reddish-brown due to self-assembly of polymer chains (as shown in inset of Fig. 1(I)). Similar procedure was applied with the help of UV–visible analysis for rest concentrations of rr-PQT-12 solutions to compare the self-assembly of polymer chains.

2.3. Characterizations

The growth analysis in 0.125%, 0.055% and 0.026% w/v rr-PQT-12 solutions (isolated as well as aggregated) were carried out under UV–visible spectrophotometer (EPOCH2C, Biotech Instrument Inc., USA). The morphology of as-prepared fiber was characterized by atomic force microscopy (AFM, ND-MDT, NTEGRA Prima, Russia). Photo luminescence analysis was carried out on PL spectrophotometer (Perkin Elmer, LS-50B, USA). The structural

analysis of aggregated thin film was performed by X-ray diffractometer (Rigaku, SmartLab, Japan). TEM analysis was carried out at accelerating voltage of 200 kV on FEI Techai, (G² F20 twin, Swiss Republic). Electrical measurements were carried out using a Keithley dual channel system source meter (model 2612A) by making a proper biasing with the help of a four probe station (model PE-4RF, Everbeing, Taiwan).

3. Results and discussion

It is previously reported that due to numerous conformational degree of freedom and segmental partially filled sp^2 hybrid orbitals (loosely bound π -orbitals); conducting polymers tend to self-assemble into a favorable microstructure that mainly depends upon applied conditions [28]. Particularly, in solution state, due to low saturating concentration, these polymers are capable of self-assembly when subjected to a gradual decrement in temperature. Herein, individual unimers act as template for the other molecules [29]. Similar to rr-P3HT, there are two types of self-assemblies can also be possible for rr-PQT-12 viz. one along a-axis and other along b-axis which is abbreviated as H and J aggregation respectively (as schematically represented in Scheme 1) [22–24]. On the other hand, chain folding plays crucial role for the conformation of individual unimers. For example, rr-PQT-12 exhibits loosely packed aggregated chain conformations into fiber than rr-P3HT due to rigidity of quarter thiophene backbone [30]. That is why, rr-P3HT shows aggregation by folding of chains while PQT-12 exhibits non folding aggregation into fiber. Herein, we are studying charge transport properties of non-folded rr-PQT-12 fiber compared to its isolated analogue by various tools

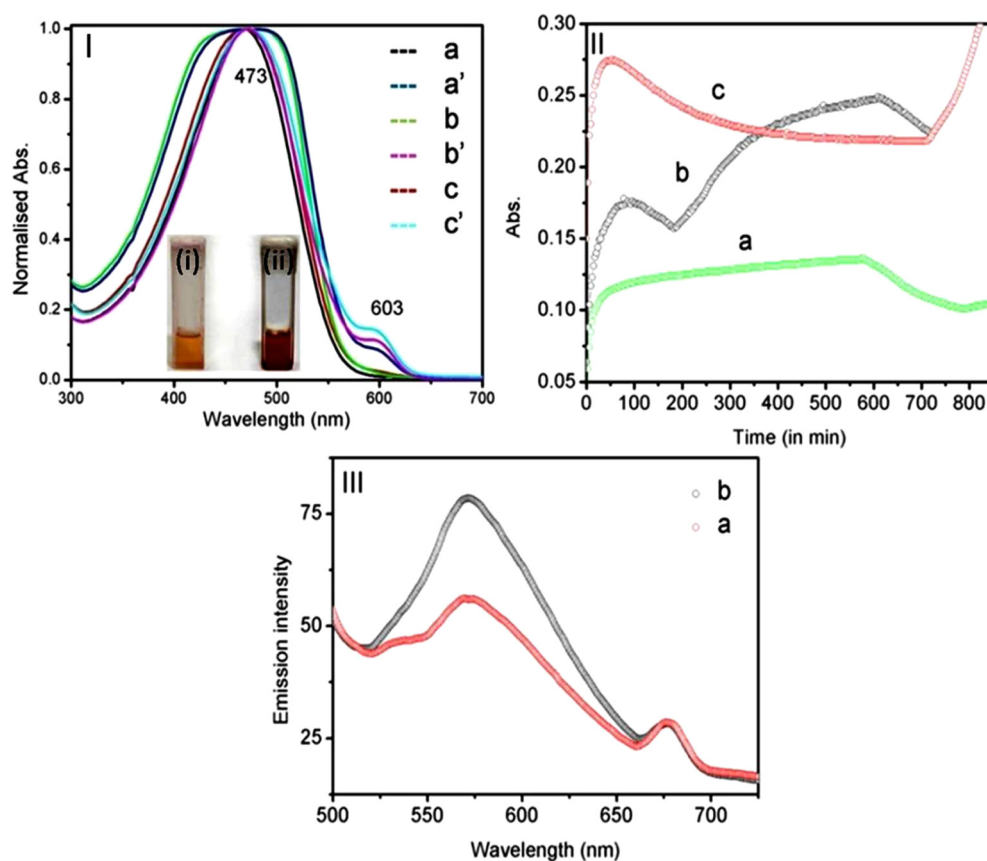


Fig. 1. (I) UV–visible analysis of isolated (a, b and c) and aggregated (a', b' and c') rr-PQT-12 for 0.026%, 0.055% and 0.125% w/v respectively, (II) Time dependent absorbance analysis of (a) 0.026% w/v, (b) 0.055% w/v and (c) 0.125% w/v in chloroform and (III) PL of (a) aggregated and (b) isolated rr-PQT-12 excited at 473 nm. Inset of Fig. 1I represents photograph of change in color of rr-PQT-12 solutions from zero time (isolated) and after 45 min ageing (aggregated) marked as (i) and (ii) respectively.

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