High-Performance Semiconducting Polythiophenes for Organic Thin-Film Transistors

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Organic thin-film transistors (TFTs) have attracted intense research interest in recent years.[1–11] First, their potential for fabricating very low-cost integrated circuits[2–5] for large-area electronic devices (e.g., active matrix displays), where use of current silicon technology can be prohibitively costly, has been the primary motivation. Second, their compatibility with plastic substrates[2,6] has rendered them ideal for creating compact, lightweight, mechanically flexible, and structurally inspiring electronic device designs (e.g., electronic papers). To enable low-cost manufacturing, circuit fabrication using simple solution techniques[7] under ambient or nonsterile conditions is highly desirable. However, currently known solution-processable semiconducting polymers provide poor transistor properties (e.g., low mobility, low current on/off ratio, etc.) when the semiconductors are deposited in air. For example, TFTs fabricated in air with regioregular head-to-tail poly(3-hexylthiophene), P3HT, generally exhibited much lower performance characteristics[8] than those fabricated in an inert atmosphere.[4] This was primarily due to the sensitivity of regioregular P3HT to atmospheric oxygen. On the other hand, the relatively air-stable poly(9,9′-dioctyl-fluorene-co-bithiophene) achieved a mobility of only $0.01-0.02$ cm^2 V^{-1} s^{-1} after mechanical rubbing of substrates and very high-temperature annealing.[9] The difficulty in attaining desirable transistor functionality in semiconducting polymers under ambient conditions is primarily due to (i) fundamental structural deficiency in the ability to achieve proper structural orders in thin films and energetics for efficient charge carrier transport[4] and/or (ii) sensitivity to chemical doping by atmospheric oxygen, resulting in increased free carrier density, which degrades performance.[8,10]

We report here a class of solution-processable regioregular polythiophenes, poly(3,3′′′-dialkyl-quaterthiophene)s, **2** (PQTs), that affords excellent TFT performance under ambient conditions. No precautionary measures need to be taken in excluding oxygen, moisture, or light during device fabrication. This class of polythiophenes was designed on the basis of the following structural considerations: (i) appropriately long alkyl side-chains for solution processability; (ii) structural regularity to induce and facilitate molecular self-assembly; and (iii) proper control of extended π-conjugation to achieve a delicate balance between transistor functionality and oxidative doping stability.

The oxidative doping of semiconducting conjugated polymers depends on their ionization potentials (IPs), i.e., their highest occupied molecular orbital (HOMO) levels from vacuum, which are dependent on their effective π-conjugation lengths. For polythiophenes, coplanarity of the thienylene moieties along the polymer chain leads to extensive π-conjugation and, thus, a lower IP, and a greater propensity to be oxidatively doped. Deviations from coplanarity result in shorter effective π-conjugation lengths, higher IPs, and greater resistance against oxidative doping. We have found that both torsional barriers and rotational freedom of thienylene moieties can be utilized in tuning π-conjugation to simultaneously

Scheme 1
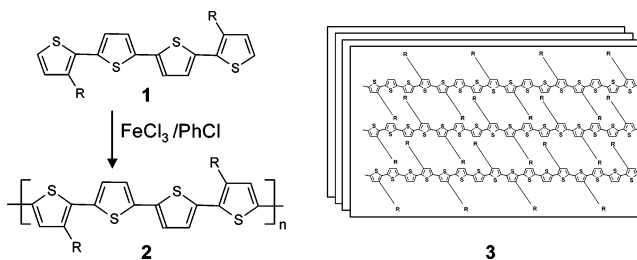
achieve both TFT functionality and oxidative stability in a polythiophene system.[11]

In PQT, **2**, the alkyl side-chains are strategically positioned along the polythiophene backbone such that the repeating length of the polymer is about 15.5 Å. Those side-chains oriented in the same directions in the extended polymer conformation are spaced approximately 12 Å apart as they are tilted at an angle ∼50° against the backbone. This 12 Å spacing, together with a sufficiently long R group ($\geq C_6$), has enabled **2** to undergo self-assembly under appropriate conditions to achieve long-range intermolecular side-chain interdigitations in the condensed phase, leading to formation of three-dimensional lamellar π-stacking structural orders as schematically represented by **3**. Lamellar structures of this type had been observed in the monomeric and oligomeric forms of **2**.[12] The presence of unsubstituted thienylene moieties in PQT, which possess some rotational freedom, cuts down on the π-conjugation to an extent that imparts sufficient oxidative stability to the system. Thus, the IP of PQT was measured to be 0.1 eV higher than that of regioregular P3HT.

Compound **2** was prepared in good yields by FeClB$_{3B}$-mediated oxidative coupling polymerization[13] of quarterthiophene monomer **1** (Scheme 1) and purified by extractions with appropriate solvents. The DSC thermogram of PQT-12 (**2**, R = n-C$_{12}$H$_{25}$) showed liquid crystalline characteristics with two endotherms at ∼120 and ∼140 °C, corresponding to the crystalline-to-liquid crystalline and liquid crystalline-to-isotropic phase transitions, respectively. Similar liquid crystalline behaviors involving analogous phase transitions had earlier been observed in poly(3-alkylthiophene)s.[14] XRD of a powdered sample of PQT-12 exhibited two diffractions at 2θ = 7.4 and 21.5°, arising from side-chain (d spacing, 12.0 Å) and $\pi-\pi$ stacking (d spacing, 4.1 Å) orderings, respectively (Figure 1a). When the powdered sample was annealed at ∼120–140 °C, highly crystalline XRD patterns were observed (Figure 1b), revealing an interchain d spacing of 16.4 Å and a $\pi-\pi$ stacking distance of 3.8 Å. On the other hand, thin films of PQT-12 (∼0.2 μm) spun on a wafer modified with octyltrichlorosilane (OTS) exhibited broad XRD peaks, arising from loosely packed lamellar structures with an interchain distance of ∼18.5 Å and a $\pi-\pi$ stacking distance of ∼3.8 Å (Figure 1c). On annealing at 135 °C, very distinct crystalline diffraction peaks were observed at 2θ = 5.1° (100), 10.3° (200),
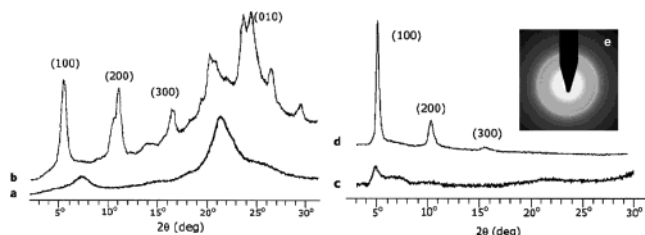
Figure 1. XRDs of PQT-12: (a) pressed pellet of precipitated polymer from polymerization; (b) pressed pellet annealed at ∼140 °C; (c) as-cast 0.2 μm thin film; (d) 0.2 μm thin film annealed at 135 °C; and (e) transmission electron diffraction pattern of PQT-12 film on carbon grid.
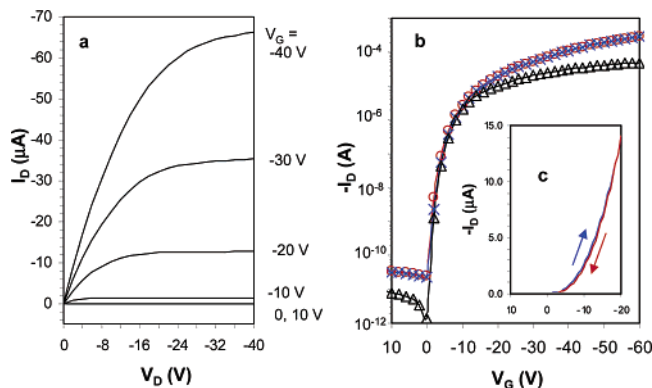

Figure 2. I−V characteristics of exemplary PQT-12 TFT device with 90 μm channel length and 5000 μm channel width: (a) output curves at different gate voltages; (b) two transfer curves in saturated regime scanned from positive to negative gate voltages (o (red) and x (blue), $V_D = -60$ V) and transfer curve at linear regime (Δ, $V_D = -6$ V); (c) two transfer curves scanned in different directions between +10 and −20 V.

and 15.4° (300) with concomitant disappearance of π−π stacking peak at $2\theta = 23.2°$ (010) (Figure 1d), manifesting the formation of highly ordered lamellar π-stacks that were oriented normal to the substrate. Transmission electron microscopic analysis of annealed PQT-12 film on a carbon grid gave a π−π spacing of 3.7 Å (Figure 1e). Accordingly, it can be concluded that PQT-12 possesses a natural ability to self-organize into highly ordered lamellar π−π stacking structures whose orientation to the substrate could be manipulated through proper alignment layers and techniques. This is reminiscent of the self-assembly exhibited by regioregular poly(3-alkylthiophene)s.[4,14b,15]

Bottom-gate top-contact TFT devices with PQT-12 semiconductor channel layers fabricated by spin coating technique under ambient conditions yielded excellent TFT properties (Figure 2). The output characteristics showed no noticeable contact resistance, very good saturation behavior, and clear saturation currents that are quadratic to the gate bias. The saturation current was more than −65 μA at the gate, and source-drain voltages were −40 V. The device switched on nicely at around 0 V, with a subthreshold slope of ∼1.5 V/decade (Figure 2a). The initial mobility was 0.02−0.05 cm² V⁻¹ s⁻¹ with an on/off ratio on the order of 10⁶. After annealing at 120−140 °C, the mobility improved to as high as 0.14 cm² V⁻¹ s⁻¹ with an on/off ratio of over 10⁷ (Figure 2b). On average, a mobility of 0.07−0.12 cm² V⁻¹ s⁻¹ was reproducibly obtained. The ability to achieve a high mobility and an extremely high on/off ratio in air attests to the significantly greater stability of PQT-12 against oxidative doping by atmospheric oxygen. The PQT-12 devices also showed only a slight decrease in mobility and on/off

ratio after being stored under ambient conditions in the dark for one month, in sharp contrast to the drastic degradation in performance of the regioregular P3HT devices under identical conditions. In addition, the mobilities for the PQT-12 device extracted from both the linear (Figure 2b) and saturated regimes were about the same, and no observable differences were noted with the top- and bottom-contact device configurations. More importantly, little or no hysteresis and bias stress effects had been observed with these devices at and above room temperature (Figures 2b and 2c). All these data suggest that PQT-12 has exhibited ideal field-effect transistor behaviors.

In conclusion, we have demonstrated that through structural design for proper self-assembly ability and controlled π-conjugation, both oxidative doping stability and excellent TFT performance characteristics can be built into a polythiophene system. To the best of our knowledge, PQT is the only conjugated polymer system that has exhibited the best all-around polymer TFT properties under ambient fabrication conditions.

Supporting Information Available: Experimental procedures, thermal analysis, and absorption spectra of PQT-12. This material is available free of charge via the Internet at http://pubs.acs.org.

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