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Phthalimide-Based Polymers for High Performance Organic Thin-Film Transistors

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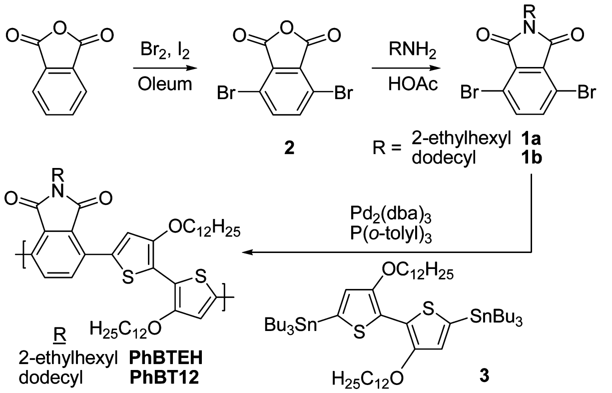
Great strides have been made over the last 5 years to develop conjugated polymer (CP) based organic thin film transistors (OTFTs) with ambient operational stability. A benchmark polymer, regioregular poly(3-hexylthiophene) (rr-P3HT),[1] can provide hole mobilities of ~0.1 cm^2/(V s) and a current modulation $\geq 10^5$, close to amorphous silicon, but only under inert atmosphere. A successful strategy toward increased ambient air stability is manipulation of band energy levels by inserting other units into the polythiophene backbone.[2] Ionization energies can be elevated by increased backbone torsion, or greater electron localization. However, polymer-based OTFTs with extended ambient operational stability remain a rarity.[3]

The strongly electron-withdrawing imide groups of arylene imides should largely alter band energy levels when inserted into polythiophene backbones. A few published examples include polymers containing thiophene imides,[4] bithiophene imides,[5] isothianaphthene imides,[6] and rylene imides.[7] The latter three classes of polymers have led to moderately efficient solar cells, OTFTs with moderate to excellent performance, and charge-storage media. The only reported CPs with backbone phthalimide units appear to be poly(phenylene ethynylene)s[8a] and a polyaniline derivative.[8b] 3,6-Dibromo-phthalimides are attractive candidates for electron-accepting comonomers due to their extremely facile synthesis and readily varied substitution at the imide nitrogen, allowing manipulation of polymer solubility, packing, and morphology.

We report herein **PhBT** copolymers, which are formally the product of insertion of phthalimide into the repeating unit of poly(3,3′-dialkoxy-2,2′-bithiophene) and their unoptimized OTFTs under ambient conditions, which are among the best for polymer semiconductors. The influence of the phthalimide units on frontier molecular orbital energy levels, polymer packing, and thin film morphology should depend strongly on the degree of torsion between the backbone repeating units. Backbone planarity is likely enforced here by attractive intramolecular interactions between pendant oxygens and thienyl sulfur atoms,[9] intermolecular donor−acceptor interactions, and possibly increased quinoidal backbone character due to alternating donor and acceptor units.[10]

Phthalimide monomers **1a/b** are easily prepared in two steps from commercially available starting materials (Scheme 1). Stille copolymerization with bithiophene **3** leads to high molecular weight polymers **PhBTEH** and **PhBT12** in ≥90% yield. ^{1}H NMR spectra and elemental analysis indicate high purity and molecular weight. GPC measurements gave number-average molecular weights of 117.3 kDa (**PhBTEH**) and 207.5 kDa (**PhBT12**) vs polystyrene standards. Differential scanning calorimetry reveals irreversible endotherms for both between 330 and 360 °C (Figure S10), near the onset of thermal decomposition detected via thermogravimetric analysis (Figure S11).

Scheme 1. Synthesis of Phthalimide-Bithiophene (PhBT) Polymers



The thin-film absorption profiles for both polymers are nearly identical and broad/featureless with $\lambda_{max} = 614$ nm (Figure S9). This is red-shifted by ~50 nm relative to dilute $CHCl_3$ solutions, indicating increased backbone planarization and π-stacking in the solid state.[11] Low-energy shoulders appear after annealing the films at 200 °C. The shoulder is more distinct for **PhBT12** and extends to a longer wavelength, in agreement with X-ray diffraction (XRD) studies described below. Optical energy gaps (E_g^{opt}) estimated from the onset of absorption are 1.72 eV (**PhBTEH**) and 1.64 eV (**PhBT12**). Though many factors may contribute to these fairly low energy gaps, relatively extended conjugation along the donor−acceptor polymer backbones can be assumed. Insertion of phthalimide into the repeating unit of poly(3,3′-dialkoxy-2,2′-bithiophene) apparently has little effect on E_g^{opt} (~1.65 eV for parent).[9d,e] However, the onset of oxidation (cyclic voltammetry, Figure S8) for **PhBT** is ~0.8 V more positive than that reported[9d] for the parent polymer, indicating a shift of 0.8 eV for the HOMO, and LUMO as well, since E_g^{opt} is unchanged. Measured under the same conditions, the oxidation potentials of the **PhBT** polymers were ~0.1 V more positive than that of rr-P3HT (Figure S8). This should impart increased ambient stability to transistors fabricated from the new polymers.

The charge-transport properties of the polymers were investigated by fabricating OTFTs with the most basic architecture: bottom gold contacts, bottom gate, and SiO_2 dielectric, similar to our previous reports.[2b,12] All devices were fabricated and tested in ambient air and light without special precautions. The devices showed good current modulation and well-resolved linear and saturation currents in the p-channel response as shown in Figure 1. Average device characteristics are taken from over 30 devices for each polymer.

Calculated maximum field-effect mobilities were 0.28 cm^2/(V s) for **PhBT12** and 0.036 cm^2/(V s) for **PhBTEH** in the

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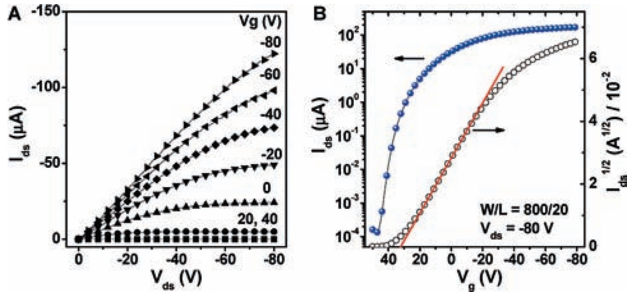

Figure 1. (A) Output and (B) transfer characteristics of PhBT12 thin-film transistor under ambient conditions.

saturation region. On/off current ratios of 10^4-10^5 were routinely observed from both polymers with maximum values greater than 10^6. Average threshold voltages were 24 V for **PhBT12** and 31 V for **PhBTEH**. Average hole mobilities of **PhBT12** and **PhBTEH** were 0.17 (±0.05) and 0.017 (±0.008) cm^2/(V s), respectively. However, like nearly all polymers that have shown improved initial ambient stability relative to rr-P3HT, charge-carrier mobilities and current modulation degraded over time in air. Drastically improved operational stability over extended periods was observed[3] from PBTTT-based OTFTs after varying device fabrication parameters, and we will report on such studies with **PhBT** in the future.

X-ray diffraction (XRD, Figure 2) measurements reveal first- and second-order diffraction maxima at intermediate angles, indicating short-range lamellar ordering after these fabrication conditions. Wider-angle diffraction maxima are assigned to the π-stacking distances for **PhBT12** (3.6 Å) and **PhBTEH** (3.7 Å). Contrary to *d*-spacings from single-crystal diffraction measurements, these values are upper limits, possibly differing merely due to such phenomena as differing angles between the backbone ring planes and the π-stacking axes. However, **PhBT12** gives an apparently more distinct peak suggesting longer-range correlation, possibly linked to differences in thin-film UV/vis absorption profiles and OTFT performance. For comparison, 2D-diffraction patterns collected in transmission mode from thermally annealed, extruded fibers of both polymers indicate longer-range order with three-dimensional registry (Figure S12).

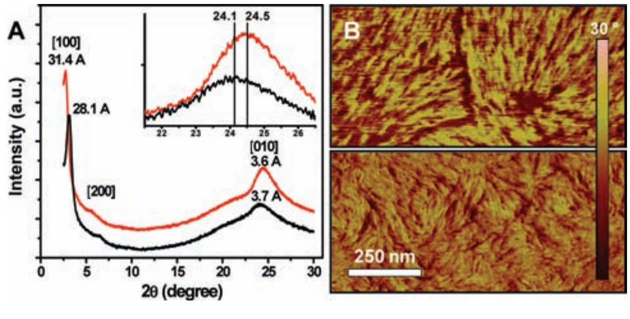

Figure 2. (A) Film XRD of PhBTEH (black) and PhBT12 (red). (B) AFM phase images of PhBTEH (top) and PhBT12 (bottom).

Atomic force microscopy (AFM) images collected from the devices reveal fibrillar ordered domains with widths of 15−30 nm (Figure 2B; S13). Domain boundaries are not as well-resolved in thin films from **PhBT12** as from **PhBTEH** (Figure 2B). The better performance of the former might then be attributed to more extensive domain interconnectivity.[13] Finally, direct correlations have been drawn between molecular weight, thin film morphology, and OTFT performance of rr-P3HT.[14] The relative molecular weights of the two **PhBT** polymers seem to be sufficiently high that their differences would not contribute to their differing device performance, but this possibility cannot be excluded.

In summary, phthalimide units may be incorporated into thiophene polymer backbones exhibiting extended conjugation and π-stacking. Basic solution processing techniques provide films with ordering sufficient for OTFT mobilities of ~0.2 cm^2/(V s) under ambient conditions without optimization. The absorption and charge-carrier characteristics of the **PhBT** polymers also contribute to good performance in photovoltaic devices, to be reported elsewhere.

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Supporting Information Available: Details of materials synthesis/characterization and OTFT fabrication/characterization. This material is available free of charge via the Internet at http://pubs.acs.org.

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