Communication

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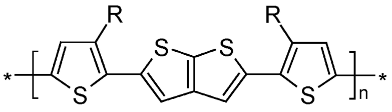

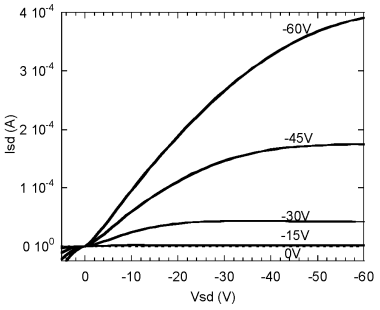

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Stable Polythiophene Semiconductors Incorporating Thieno[2,3-*b*]thiophene

Martin Heeney, Clare Bailey, Kristijonas Genevicius, Maxim Shkunov, David Sparrowe,
Steve Tierney, and Iain McCulloch*

Merck Chemicals, Chilworth Technical Centre, Southampton, United Kingdom

Received November 16, 2004; E-mail: iain.mcculloch@merckchem.co.uk

Polythiophenes have been widely studied due to their attractive electronic and optical properties.[1] An interesting application is the use of these materials as the active semiconducting layer in organic field effect transistors (OFETs) where solution processability can be exploited in the fabrication of large area, low cost, flexible devices.[2] In particular, regioregular head-to-tail poly(3-hexylthiophene) (P3HT) has shown some of the highest charge carrier mobilities reported for any soluble polymeric system.[3] A primary reason for this is the crystalline nature of the thin films obtained from solution, where the polymers self-organize by assembly of the side chains to afford well-ordered lamella with cofacially stacked polymer backbones. The resulting small cofacial distances (3.8 Å) give rise to efficient charge carrier hoping.[4] However, one drawback of fully conjugated thiophene polymers is that in some transistor architectures, the electrical performance in air can be poorer than the performance under inert atmosphere.[5] This is attributed to unintentional p-type doping of the semiconductor by interaction with oxygen, which is a redox dopant. Doping changes the transistor characteristics, typically increasing the off current and shifting the threshold voltage. Although several recent publications have demonstrated the long-term performance of P3HT transistors,[6] some applications, such as organic TFTs in display backplanes,[7] demand a higher on/off ratio, and hence there is a strong requirement for air stable semiconductors.

The stability of a polymer toward oxidative doping can be improved by increasing its ionization potential (accomplished by lowering the HOMO level with respect to vacuum). This is dependent, among other factors, on the effective π conjugation length of the polymer backbone, which can be controlled either sterically, by reducing π overlap between adjacent thiophene rings, or electronically by introducing a non or less conjugated unit into the backbone, thereby inhibiting delocalization. Twisting adjacent thiophene rings can be achieved by steric crowding, for example head-to-head 3-alkyl linkages on neighboring thiophene rings. This approach however tends to also inhibit packing, resulting in low mobilities. An alternate approach is to reduce π overlap by increasing the rotational freedom of the backbone.[8] Preventing delocalization can be most readily achieved by introducing a nonconjugated comonomer. However, the introduction of a sp^3-hybridized unit into the backbone can also introduce undesired conformational effects and bend the backbone out of plane.

In this paper, we report on an alternative approach whereby delocalization of the π electron system is disfavored by the incorporation of an aromatic heterocycle that cannot form an extended conjugated pathway with both of its neighboring coupled monomer units. The heterocycle thieno[2,3-b]thiophene (**1**) was chosen and coupled in the 2,5-positions within the backbone, as shown in Scheme 1. In this approach, a planar backbone conformation can be achieved, thus preserving the close $\pi-\pi$ intermolecular distances necessary for high charge carrier mobilities. The resulting solution processable polymers (**2**) exhibit excellent TFT performance under ambient conditions.

Scheme 1

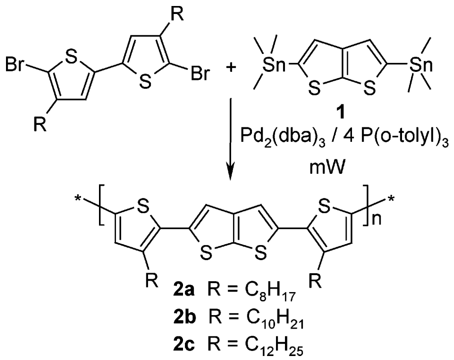

Table 1. Summary of Physical, Thermal (second heating cycle), and Electrical Characteristics

R	M_n (g/mol)	D	T_{DSC} (°C)	λ_{MAX} (film/nm)	max μ (cm^2/V s)
2a	15 000	2.3	41, 184.5	467	*a*
2b	29 000	2.0	17, 183.5	470	0.15
2c	26 000	1.9	15, 184	472	0.12

[a] Not measured due to low polymer solubility.

Thieno[2,3-*b*]thiophene is a stable aromatic heterocycle readily synthesized in high yield.[9] Due to the central cross-conjugated double bond, it is unable to form a fully conjugated pathway between substituents at the 2,5-position. A series of regiosymmetric copolymers with 4,4-dialkyl 2,2-bithiophenes were prepared by Stille coupling (Scheme 1). The regiosymmetric arrangement of the chains shown in **2** both facilitates a range of possible polymerization methodologies and is necessary to avoid head−head alkyl couplings, which would disrupt a planar backbone conformation. The polymerizations were performed under microwave heating, resulting in improved molecular weights and reduced reaction times compared to conventional heating.[10] The resulting polymers exhibited good molecular weights and low polydispersities (Table 1). Alkyl chains promote self-organization in the solid state, and chain lengths of decyl and longer were necessary to ensure good solubility in a range of ‘printing friendly’ solvents.

The absorption spectrum of **2b** exhibits an absorption maximum at 421 nm in solution and 470 nm in the solid state (Figure S1). This is a large hypsochromic shift compared to P3HT, which has a maximum absorbance at 560 nm in the solid state, and is consistent with a reduction in the effective conjugation length. Polymer **2b** was observed to have an ionization potential of 5.3 eV as a thin film, as determined by a UV photoelectron spectroscopic technique.[11] Regioregular P3HT, measured for comparative purposes by the same technique, had a value of 4.8 eV. The bathochromic shift of **2b** from solution to solid state and the observation of a longer wavelength shoulder at 500 nm are

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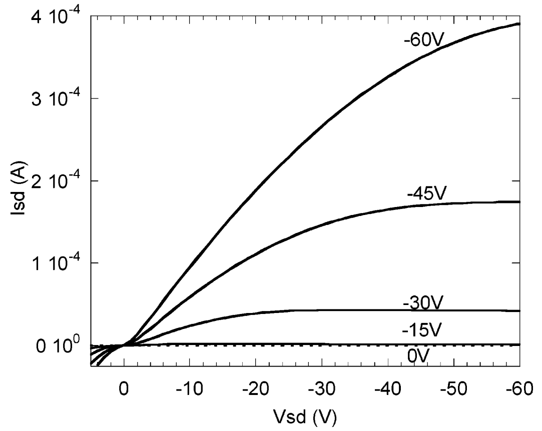

Figure 1. Output characteristics of **2b** in air scanned at different gate voltages.

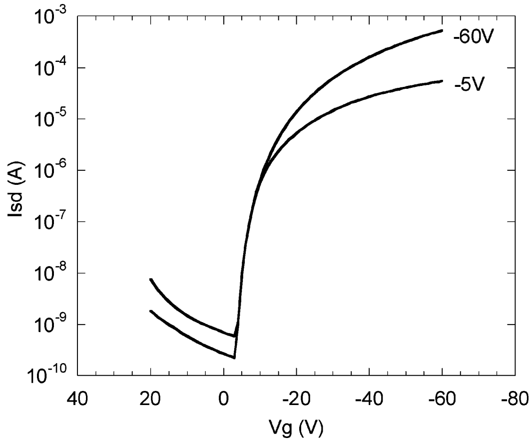

Figure 2. Transfer characteristics of **2b** in air scanned from positive to negative gate voltages at drain voltage of −5 V and −60 V.

indicative of aggregation in the solid state. The DSC thermograms of all polymers **2** show two endotherms on heating (Figure S2). A broad endotherm around room temperature is followed by a polymer melt to an isotropic phase around 180 °C. These transitions are attributed to side chain and backbone melting, respectively. Upon cooling, a sharp exotherm is observed, accompanied by the formation of birefringent texture under crossed polarizers. The high-temperature endo- and exotherms are reversible, and the temperature at which the exotherm occurs on cooling is relatively independent of cooling rate, suggesting the polymer is entering a liquid crystalline phase. Preliminary wide-angle X-ray scattering measurements of spin coated thin films of **2b** indicate lamellar films with an interlayer spacing of 17 Å and a $\pi-\pi$ stacking distance of 3.7 Å.

Thin film transistors employing polymer **2b** or **2c** were fabricated by either spin coating or drop casting dichlorobenzene or xylene solutions onto bottom gate, bottom contact substrates. Both methods gave similar results. Devices were annealed between 100 and 125 °C prior to measurement, typically improving mobilities by up to a factor of 2. The devices showed classical p-type behavior, with good current modulation and well-defined linear and saturation regimes, even at short channel lengths. The output characteristics, shown in Figure 1, show slight nonohmic resistance at low source−drain voltages, most probably due to the 0.3 eV mismatch between the work function of Au and the HOMO of **2** (−5.3 eV).

The devices switch on at a gate voltage of around −3 V (Figure 2), with a subthreshold slope of 1.2 V/decade. Saturated mobilities between 0.01 and 0.05 cm^2/V s are routinely obtained with 10 μm channel length transistors. Mobilities up to 0.15 cm^2/V s are achieved at shorter channel lengths (5 and 3 μm), most probably due to the increased longitudinal electric field across the channel.[12] On/off ratios of 10^5 are routinely achieved in air, with little degradation observed in the electrical characteristics over time upon storage in ambient atmosphere and light (wavelengths <500 nm removed by filtration, Figure S3).

In conclusion, a new design methodology was employed to create aromatic polymers with well-defined conjugation lengths through coupling in the nonconjugating positions of the fused heterocycle thieno[2,3-*b*]thiophene. The polymers described show both good charge carrier mobility and stability to ambient air and light.

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Supporting Information Available: Experimental procedures and detailed information about the fabrication and measurement of TFTs. This material is available free of charge via the Internet at http://pubs.acs.org.

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