Highly Conductive, Regioregular Alkoxy-Functionalized Polythiophenes: A New Class of Stable, Low Band Gap Materials

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Electrically conductive polymers are entering a new era as devices and applications are beginning to enter the marketplace. Decades of revolutionary research has not only created exciting new science but also led to new plastic electronics.1 Due to very high electrical conductivities, regioregular polythiophenes (r-PTs) are being used in plastic photovoltaics, as the hole transport layer in OLEDs, in field effect transistors, and as conductive components in new coatings and bulk plastics.2,3 Alkoxy-substituted analogues of PTs exhibit even more desirable properties, such as reduced band gaps, low oxidation potentials, and a highly stable conducting state.4-6 However, these materials possess rather low conductivities (1 S/cm) and are not very stable. A major breakthrough in the development of the commercially viable conductive polymers was the synthesis of poly(3,4-ethylenedioxythiophene) (PEDOT), which exhibited high stabilities in the oxidized state and conductivities up to 600 S/cm.7-9 Unfortunately, this material is generally only processible as a colloidal suspension in water and produces fairly low conductivities (10-50 S/cm), thereby limiting its usefulness in many commercial applications. Nevertheless, since the discovery of PEDOT in 1989, dioxithiophene chemistry has developed exponentially and has rapidly

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become the frontier of PT-based inherently conductive polymers (ICPs). The pioneering work of Reynolds has led to regiosymmetric PXDOTs including the first soluble, very stable dialkylation poly(3,4-propylene dioxythiophenes) (PXDOT-R) that exhibit moderate conductivities (e.g., 7 S/cm, for chemically prepared samples) and possess excellent redox and electrochemical properties.\(^9\) Despite these discoveries, generating materials that possess high carrier mobilities and long-term stabilities in the oxidized state and are easily processible remains a great challenge. Here we present the synthesis and unique physical properties for a new class of regioregular 3-alkoxy functionalized polythiophenes that exhibit high electrical conductivities and very good stabilities when doped with iodine vapor followed by exposure to ambient conditions. In addition, we present air doping of the polymers by atmospheric oxygen.

For the first time, a series of soluble structurally regioregular alkyloxy-substituted PTs (>98% head-to-tail (HT) couplings) of high molecular weights was synthesized through the Grignard Metathesis (GRIM) method,\(^1\) which utilizes a chain-growth nickel complex-initiated cross-coupling reaction.\(^12\) Previously, 3-hexyloxythiophene (HOT, 2a) and 3-[2-(2-methoxyethoxy)ethoxy]thiophene (MEET, 2b) monomers were polymerized via an oxidative chemical polymerization with ferric chloride (FeCl3).\(^6\) However, the resulting materials were regioirregular oligomers of low molecular weight (1387 and 860 for 2a and 2b, respectively). Furthermore, higher molecular weight fractions of these polymers were insubile and insoluble solids due to cross-linking via \(\alpha,\beta\) couplings between thiophene rings.

In this work, dibromoalkoxythiophenes monomers (1a–d) were synthesized in 80–90% yields first by copper (I) mediated substitution of 3-bromothiophene,\(^13\) followed by a modified NBS bromination\(^14\) in THF at cryogenic temperatures. The polymerization involved treatment of 1a–d with a Grignard reagent R'MgX (e.g., MeMgBr) that resulted in magnesium bromine exchange, generating a mixture of regiochemical Grignard isomers.\(^15\) Investigation of the reaction mechanism employing kinetics revealed that, upon addition of Ni(dppe)Cl2, the polymers were formed by the selective coupling of 2-bromo-5-halomagnesio-3-alkoxy-thiophene followed by 2-halomagnesio-5-bromo-3-alkoxy-thiophene to afford HT-coupled regioregular polymers (2a–d) in good yield (e.g., 60–70%) (Scheme 1).\(^15\)

The polymerization of 1a generates PHOT (2a) in high yield (>80%). The fraction of 2a that was soluble in chloroform was a rather low molecular weight \((M_w = 7200; M_n/M_w = 1.7)\). Polymerization of 1b yielded PMEET (2b) with a relatively high molecular weight \((M_n = 18000; M_w/M_n = 1.6)\). Since the polymerization proceeds by a chain growth mechanism,\(^12\) polymers of alkyloxy-substituted thiophenes of varying molecular weights could be easily synthesized. Moreover, incorporation of several oxygen atoms in a polymer backbone (e.g., 2b–d) resulted in polymers that were readily soluble in many common organic solvents relative to 2a\(^6\) and possessed excellent film-forming abilities. As an example of characterization, the \(^1\)H NMR spectra of PMEET (2b) revealed only one aromatic resonance with a chemical shift at \(\delta = 6.98\) ppm, as expected for a regioregular PT\(^17\) and only four resonances (\(\delta = 111.4, 112.9, 132.2,\) and 153.2 ppm) in the aromatic region in the \(^{13}\)C NMR spectrum. The UV–Vis data for PMEET (2b) showed a \(\lambda_{max}\) of 602 nm in CHCl3 solution and \(\lambda_{max}\) of 685 nm \((E_g = 1.41\) eV\) in the solid state as drop cast from CHCl3.

As a comparison, the \(\lambda_{max}\) values obtained for electrochemically prepared films of PEDOT were 580–610 nm \((E_g = 1.60\) eV\).\(^18\)

Thin films of 2a–d were generated by the slow evaporation of CHCl3 solutions and were doped with iodine. The conductive properties of the films stabilized over several weeks and remained more or less unchanged. The thin films of oxidized polymers were green initially, and upon diffusion of iodine from the polymer, the color changed to near transparent sky-blue. The films of PMEET (2b) exhibited very high average electrical conductivities of around 200 S/cm, with some samples exhibiting maximum conductivities of 650 S/cm (Figure 1).\(^15\) The SEM analyses revealed that the most conductive films were of exceptional quality and very dense.\(^12,18\) One of the most amazing findings was that PMEET (2b) is extremely stable to ambient conditions and remains highly conductive over long periods of time. The electrical conductivity of a cast film of 2b, which was oxidized with iodine for 12 h followed by exposure to ambient conditions, was originally at 93 S/cm (Figure 1). Subsequently, a dramatic increase in conductivity (up to 650 S/cm) was observed within 24 h. Upon gradual diffusion of

\(\text{Scheme 1. Synthesis of Regioregular Alkoxy-Functionalized Polythiophenes by the Grignard Metathesis (GRIM) Method}\)

\[\begin{align*}
\text{Br} & \quad \text{Br} \\
\text{1a–d} & \quad \text{Ni(dppe)Cl}_2, 12h \\
\text{2a–d} & \quad \text{CH}_2\text{OH}
\end{align*}\]
iodine from the polymer matrix, the conductivity remained almost constant at 150 S/cm after allowing the iodine adduct to stand at room temperature for over 2 months in air. Prior to optimization of film formation, we had prepared several iodine oxidized cast films of 2b that were kept at ambient conditions for over 3 years and these films still had conductivities of 25–35 S/cm (Table 1).

The increase in the conductivity over time was possibly due to either doping with atmospheric oxygen or the release of excess iodine from the polymer. Excess iodine could cause charge pinning or initial disruption of the conjugation system due to overoxidation, in which the placement of iodine ions along the chains could lead to distortion of the intermolecular order and reduction of interchain charge transfer, as previously reported by Reynolds. Preliminary thermal stability tests indicated that iodine-doped PMEE (2b) was stable when exposed to 70 °C for 2 days under ambient light and atmosphere. Samples with conductivities of 20 S/cm showed only slight drops in conductivity to about 10 S/cm and then remained stable for months. In contrast, conductivities of iodine-doped poly(3-alkylthiophene) decrease by a factor of 1000 to 10000 over time. Due to their low oxidation potential, the polymer films could be oxidized by atmospheric oxygen. For example, “air-doped” PMEE (2b) exhibited conductivities of 0.1–10 S/cm in thin films (50–200 nm).

<table>
<thead>
<tr>
<th>Conductivity (S/cm)</th>
<th>1 min</th>
<th>24 hrs</th>
<th>30 days</th>
<th>3 yrs</th>
</tr>
</thead>
<tbody>
<tr>
<td>PHOT (2a)</td>
<td>0.1</td>
<td>3</td>
<td>2</td>
<td>0.15</td>
</tr>
<tr>
<td>PMEE (2b)</td>
<td>4</td>
<td>14</td>
<td>25</td>
<td>35</td>
</tr>
</tbody>
</table>

The conductivity of 150 S/cm after allowing the iodine to stand for 5 days and 0.2 S/cm after more than 3 years of exposure to ambient conditions. Polymers 2c and 2d exhibited conductivities of up to 50 S/cm and up to 0.5 S/cm when iodine- and air-doped, respectively.

The polymers 2b and 2d were oxidized in solution with different dopants, such as I2, NOPF6, and ZnCl2. Upon successive additions of I2 and NOPF6, the π to π* transition was depleted, giving rise to two lower energy transitions at 1100 nm and near 1600 nm, respectively. The neutral polymer solution of 2b was dark purple (dark blue for 2d) in color and, upon slow oxidation, the solution first turned blue, then sky blue, almost transparent, and eventually green. At high doping levels, the UV–Vis–NIR spectra exhibited a single strong electronic absorption, indicating formation of bipolarons and displaying characteristics of the free-carrier absorption of the metallic state. One very interesting observation was that solutions treated with excess ZnCl2 caused the polymer solution to become transparent and doped. It is possible that the zinc(II) could have been inserted within the alkoxy side chains, leading to a supramolecular organization of the polymer. It was noted that the polymers in their oxidized form could remain in solution for extended periods of time, and allowing for the self-organization of the conjugated polymer backbones before being processed.

These regioregular poly(3-alkoxythiophenes) are remarkable new materials that are very stable, processable, and highly conductive. It is our hope that they may bring further commercialization of conductor polymers closer to reality.

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Supporting Information Available: A complete description of the procedures for the synthesis of the monomers and the corresponding polymers are available (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.