Toward Tuning Electrical and Optical Properties in Conjugated Polymers Using Side Chains: Highly Conductive Head-to-Tail Heteroatom-Functionalized Polythiophenes

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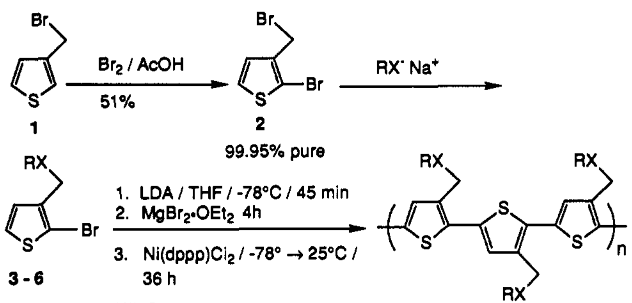
Understanding of the effects of fundamental molecular structure on material characteristics in conducting polymers[1] requires the construction of materials with very well-defined physical structures.[2] Efforts to prepare regioregular head-to-tail (HT) poly(3-alkylthiophenes)[3] (PATs) led to the development, in our lab[4] and then elsewhere,[5] of a method for the chemical polymerization of 3-alkylthiophenes that provides essentially 100% HT couplings.[4] These self-orienting PATs were used to elucidate the structure–property relationships in this class of conducting materials.[6] We are now able to tune the electrical and optical properties in conjugated polymers. We present the synthesis and unique physical properties for a series of the first HT heteroatom functionalized polythiophenes[7,8] with high electrical conductivities. These results demonstrate the compatibility of the polymerization method with functional groups and the use of side chains to control conjugation lengths.

Scheme I. Synthesis of Head-to-Tail-Coupled, Heteroatom-Substituted Polythiophenes



XR Group		
3 & 7	$-OCH_2CH_2OCH_2CH_2OCH_3$	**HT-7**
4 & 8	$-OCH_2CH_2OCH_3$	**HT-8**
5 & 9	$-OCH_3$	**HT-9**
6 & 10	$-SCH_3$	**HT-10**

Bromination[9] of **1**[10] leads to 2-bromo-3-(bromomethyl)thiophene (**2**) in a 51% yield (>99.95% pure). Molecules **3–6** were prepared in high yield (73–88%) by simple nucleophilic substitution of the general precursor **2** (Scheme I). The polymerization of **3** with a catalytic[11] amount of Ni(dppp)Cl_2 yields HT-poly[3-(2,5,8-trioxanonyl)thiophene] (**HT-7**) in 65% yield which contains 99% HT couplings. **HT-7** has a M_w of 71 000 (≈160 rings/chain, PDI = 2), as determined by GPC (relative to polystyrene), and is the highest molecular weight HT conducting polymer prepared to date. In addition, lower molecular weight polymers of HT-poly[3-(2,5-dioxahexyl)thiophene] (**HT-8**), HT-poly[3-(2-oxapropyl)thiophene] (**HT-9**), and HT-poly[3-(2-thiopropyl)thiophene) (**HT-10**) can be prepared[4] using this procedure (Scheme I). This method differs from our synthesis of HT PATs in that each step was carried out at −78 °C.

^1H NMR examination of **HT-7** shows *only* one singlet at 4.66 ppm. This peak represents the methylene protons on the first carbon of the 3-substituent.[8a] In addition, ^{13}C NMR shows *only* four resonances in the aromatic region, corresponding to the four carbons of the thiophene ring repeating unit with HT structural type (>99% HT).[2c]

Electronic absorption spectra[4] on the **HT-7** show a solution ($CHCl_3$) λ_{max} = 439 nm and a solid state λ_{max} = 486 nm. The polymer **HT-7** exhibits marked solvachromism.[1c,12] When dissolved in 1:1 CH_3CN:CH_2Cl_2, the material shows a 30-nm red shift (λ_{max} = 469 nm) relative to the λ_{max} in $CHCl_3$. In addition, it was surprising to find that while **HT-7** was completely insoluble in CH_3CN, the polymer dissolved in a solution of CH_3CN which contained $LiBF_4$. The addition of salt also changed the absorption spectrum. The new λ_{max} was 458 nm for **HT-7** in a 1:1 CH_3CN:CH_2Cl_2 solution containing 0.1 M $LiBF_4$. The addition of salts affects the conformational state of the polymer through complexation of lithium by the side chains.

Cyclic voltammetry of thin films of **HT-7** shows two reversible oxidations at very low potentials ($\Delta E_{1/2}(1)$= +0.59 V, $\Delta E_{1/2}(2)$= +0.80 V).[13] Cyclic voltammetry of a thin film of HT-poly(MEEMT) in both 0.2 M $(n\text{-hexyl})_4NBF_4$ and 0.2 M $n\text{-}Bu_4NBF_4$ in CH_3CN (vs SCE) shows similar wave forms with higher oxidation potentials ($\Delta E_{1/2}(1)$= +0.66 V, $\Delta E_{1/2}(2)$= +0.88 V). This would suggest that the solid-state oxidation potential may be tuned by the selection of electrolytic salt.

Thin films of **HT-7** were generated by the slow evaporation of $CHCl_3$ solutions and were then oxidized by exposure to I_2 vapor.

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(13) Thin films of neutral HT-7 are crimson in color and become indigo upon electrochemical or chemical oxidation. Upon exposure to I_2 (3.5 h), thin films of HT-7 exhibited new absorbances representing mid-gap transitions at 1.3 and 0.77 eV. Thinner films (upon exposure to I_2 (3.5 h)) gave transitions at 1.45 and 0.65 eV. In each case, the low-energy transitions had at least double the absorbance intensity of the higher transitions. Cyclic voltammetry was performed on thin films immersed in 0.2 M Bu_4NPF_6 in CH_3CN (vs SCE).

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The electrical conductivities were immediately measured (in a dry box) by the four-point probe method. For more than 70 samples measured, conductivities ranged from 3 to 5500 S cm^{-1}. When the films[14] were *visibly* cracked, the conductivities ranged from 3 to 70 S cm^{-1} (45 samples, average $\approx$ 20 S cm^{-1}). SEM indicated that samples with conductivities of 400–550 S cm^{-1} (20–30 μm, 24 samples) had microscopic cracks. We have measured one sample with a conductivity of 5500 S cm^{-1} (20 μm) and another sample with a conductivity of 1400 S cm^{-1} (8 μm). SEM analyses of both of these films indicate that they were of exceptional quality and appeared to be dense and were neither porous *nor* cracked. One film of HT-**7** which was cast in the presence of TBAPF$_6$ exhibited a conductivity of 1300 S cm^{-1} (8 μm). Molecular modeling shows that TBA (ionic radii of 5.13 Å) fits into a "cavity" formed by two podandic arms (cavity size $\approx$ 7.9 Å). It is possible that when induced by an ion–dipole interaction between tetrabutylammonium and the podand-like side chains, an ordered structure can form.[15]

Examination of HT-**8** by ^{1}H and ^{13}C NMR and GPC shows that it is a lower molecular weight polymer (M_w = 6*K*, PDI = 2).[16] NMR analysis (^{1}H and ^{13}C) also shows the absence of undesirable couplings, and had a solid-state λ_{max} = 467 nm. Cyclic voltammetry of HT-**8** shows oxidations at $E_{pa}(1) = +0.67$ V and $E_{pa}(2) = +0.99$ V and reversible electrochromic[18] behavior. HT-**9** and HT-**10** are both brown solids with HT structure and low molecular weight. We find that where the side chain is short, the propagating species precipitates out of solution and no high molecular weight material forms.[17]

Polythiophenes with etheric side chains can now be synthesized with full regiocontrol by using the method developed for making HT-poly(3-alkylthiophenes). We are able to use molecular recognition to tune the electronic and optical properties of these highly conducting polythiophenes. In addition, this synthetic methodology will allow us to synthesize a wide variety of new substituted HT-polythiophene. We are currently pursuing such an approach.

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Supplementary Material Available: Full experimental details for the the syntheses of molecules **3**, **4**, **5**, and **6** and example polymerization (synthesis of **7**); ^{1}H and ^{13}C NMR spectra of HT polymers **7**, **8**, **9**, and **10** (both full and expanded) and both UV–vis and cyclic voltammograms for **7** and **8** (18 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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(14) Higher quality films can be produced from spin casting. Film thicknesses ranged from ~4 to 30 μm, as determined by either SEM or micrometer. The thicknesses of all of the most highly conductive samples were measured by SEM. Conductivities of this magnitude in samples of 20–25 μm are remarkable, as morphological disorder increases as film thicknesses increase, see: Yassar, A.; Roncali, J.; Garnier, F. *Macromolecules* **1989**, *22*, 804. We also feel that the regiochemical purity of these samples has extended the thin film regime from <1 μm to around 10 μm.

(15) The electrochemical synthesis of **7** in the presence of TBAPF$_6$ which led to a very highly conducting polymer could be explained by our modeling, see ref 7a. Molecular mechanics structure calculations were performed on Silicon Graphics Iris 4D using CHARMM software (Polygen, Inc.).

(16) Higher molecular weight materials are not soluble in any solvents that we have tested. In HT-poly(3-alkylthiophenes), we have found that higher molecular weight polymer is soluble only in CS$_2$.

(17) Cyclic voltammetry on thin films immersed in 0.2 M Bu$_4$NPF$_6$ in CH$_3$CN (vs SCE). Thin films of the neutral polymer are red/orange and become blue/black upon chemical or electrochemical oxidation.

(18) We have found this not to be the case for the polymerization of 3-alkylthiophenes, where the alkyl group is butyl or larger. Molecular weights are usually M_w = 10–30 K.