Design, Synthesis, and Control of Conducting Polymer Architectures: Structurally Homogeneous Poly(3-alkyli thiophenes)

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The full details of a facile synthesis of structurally homogeneous poly(3-alkyli thiophenes) (PAT’s) is presented. In three steps from 3-bromothiophene, PAT’s can be made with complete regiochemical control. We define structurally homogeneous as a regiochemically well-defined polymer structure that in our case contains almost exclusively head-to-tail couplings (HT-HT) (2,5-couplings between adjacent thiophene rings). By analysis of the NMR data, our poly(n-butylthiophene) (5a) contains 93% HT-HT couplings, 98% of the desired regiochemistry is found in poly(n-hexylthiophene) (5b), 97% in poly(n-octylthiophene), (5c), and 95% in poly(n-dodecylthiophene), (5d). Quenching studies on reactive intermediates and 13C NMR data also demonstrate the regiochemical purity of these materials. These PAT’s show lower energy absorption maximum shifts of up to 14 nm in solution, 46 nm in the solid state, and other intense lower energy peaks with shifts of up to 129 nm (609 nm) from PAT’s prepared by the usual methods. All of these data are indicative of longer mean conjugation lengths. Molecular mechanics and ab initio calculations were performed on model trimers of 3-n-alkylthiophenes and show the relationship between regiochemistry of the trimer and its resultant conformations. The results of these calculations are related to the resultant electrical conductivity in these materials. These poly(3-alkyli thiophenes) provide for the first time well-defined structures for the investigation of structure–property relationships in this class of electronic and photonic materials.

Introduction

Since the initial discovery of preparing organic polymers, chemists have sought to prepare polymers that both are soluble (and/or processable) and exhibit high electrical conductivities. Such an advancement must be made if conducting polymers are to fulfill their promise as materials for molecular electronic devices. The early problems concerning material intractability have been thoroughly addressed, and now efforts may be focused on the molecular engineering of structures in order to produce materials which possess enhanced electrical and optical properties. An effective design strategy must be aimed at controlling both the microscopic and solid-state macroscopic structure because they collectively define the resultant band structure of a given material and thereby determine its electrical and optical properties. Molecular engineering must begin with the synthesis of homogeneous structures. This is the first critical step toward the molecular engineering of organic materials that will undergo controlled macroscopic assembly and possess exceptional properties.

A clear indication of the relationship between structural homogeneity and improved electrical and optical properties is found in Naarmann polycyclopentadiene. Classical synthetic methods produce defective polycyclopentadiene with sp3-hybridized defects at junctions of cross-links between polymer chains. Given that the degree of pi overlap along the chain directly determines the band widths (and gap) and sp3 centers decrease the conjugation, classically prepared polycyclopentadiene will possess larger band gaps than a more structurally homogeneous material. Indeed, a number of theoretical studies have shown that coplanarity along the chain pi orbitals leads to better electrical properties and nonlinear optical properties. As one example, Naarmann’s defect-free polycyclopentadiene exhibits electrical conductivities close to that of copper, in the I2-doped material, and is expected to exhibit large third-order susceptibilities. It is clear that the ability to design and control conjugated pi architectures is the key to creating new advanced materials, and some elegant examples have recently appeared in the literature.


Structurally Homogeneous Poly(3-alkylthiophenes)

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We have very recently developed a synthetic route that allows for complete regiochemical control and produces, for the first time, structurally homogeneous poly(3-alkylthiophenes) (PAT's). We define structurally homogeneous as a regiochemically well-defined polymer structure that in our case contains almost exclusively head-to-tail couplings. These poly(3-alkylthiophenes) provide soluble, processable, and well-defined structures for the investigation of structure-property relationships in this class of materials. Presented herein are the full details of the synthesis of these materials, quenching studies on intermediates in the synthesis, comparative 1H and 13C NMR spectra versus classical PAT's, solution- and solid-state electronic spectra, and molecular mechanics and ab initio calculations on model oligomers of PAT's. These studies show the importance of the design, synthesis, and control of π architectures in the preparation of new advanced materials. These data show the differences between the physical properties of these PAT's and PAT's made by standard methods and give new insights into the structures of these materials. In addition, preliminary results have shown that these structures exhibit enhanced conductivities versus previously prepared materials and they are expected to show improvements in their nonlinear optical behavior.

Results and Discussion

Synthesis of Structurally Homogeneous Poly(3-alkylthiophenes). Our synthetic design strategy was to generate homogeneous structures with well-defined regiochemistry by cross-coupling target compounds such as 1 (Figure 2). The synthesis that leads to structurally homogeneous poly(3-alkylthiophenes) is shown in Scheme 1. The 3-alkylthiophenes (3) were prepared in 60-80% yields. Contrary to the regioselective bromination of 3-methylthiophene with NBS, the bromination of 3 at the 2-position requires the use of Br2 to give 4, as reported by Gronowitz. The polymerization is performed in a one-flask reaction consisting of metalation of 2-bromo-3-alkylthiophene 4 selectively at the 5-position, followed by trapping the 2-bromo-3-alkyl-5-lithiophiene with magnesium bromide etherate to afford 1. Subsequent treatment of 1, in situ with Ni(dppp)Cl2, leads to regiochemically defined head-to-tail-coupled poly(3-alkylthiophenes).

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Scheme I. Regioselectivity Synthesis of Poly(3-alkylthiophenes)

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We have applied this method in the preparation of four different alkyl-substituted polythiophenes and a few polyether-substituted polythiophenes.\(^{(17)}\) We expect that (providing that \(R\) is compatible with the coupling catalyst) this route should be general for the synthesis of a large number of poly(3-substituted thiophenes) of well-defined structure.

One of the key features of our synthesis is the ability to metallate 4 with LDA in the 5-position\(^{(18)}\) both regiospecifically and without extensive scrambling of the generated organolithium. In previous studies on thienyllithium species, we and others have found that regiospecific metalation of bromothiophenes\(^{(19)}\) and 3-alkyl thiophenes\(^{(17,20)}\) occurs either at the 2- or 5-position and not at the 4-position on thiophene. However, under certain conditions, quenching studies with water or a variety of other carbon nucleophiles have shown that scrambling may occur.\(^{(19b,c)}\) This positional exchange of the lithium and halogen on a single thiophene ring is well established and is known as the "halogen dance" mechanism. We have performed quenching studies to examine whether the 2-bromo-3-alkyl-5-thioliophiophene\(^{(21)}\) generated under these conditions undergoes scrambling and find little to no scrambling occurs. In this case, scrambling can occur by a number of pathways, including the "halogen dance" mechanism and/or a bimolecular metal-halogen exchange between the generated lithium species and the starting material 4. If the "halogen dance" mechanism occurs, quenching with TMSCl should yield 2-(trimethylsilyl)-3-butyl-5-bromo-thiophiophene and/or 2-bromo-3-alkyl-4-(trimethylsilyl)-thiophene. A bimolecular metal-halogen exchange would lead to 2-(trimethylsilyl)-3-alkylthiophene and 2,5-dibromothiophene as first-generation products. We have found that quenching with TMSCl after treatment of 4 with LDA and also after generation of the Grignard reagent (step 2 in 4 \(\rightarrow\) 5) provides \(<1-3\%\) of scrambled product.

In the case of \(R = \text{butyl}\), we have trapped the lithio species and recover only \(99\%\) of 2-bromo-3-butyl-5-(trimethylsilyl)thiophene and \(<1\%\) of 2-(trimethylsilyl)-3-butyl-5-bromothiophene as determined by \(^1\)H NMR and GC/MS. In the case of 2-bromo-3-dodecylthiophene, quenching both the Grignard and the lithio derivative and 97--98\% of 2-bromo-3-dodecyl-5-(trimethylsilyl)thiophene was obtained according to NMR and GC/MS and 2--3\% of the scrambled product by NMR. The same results are observed in quenching studies on the 3-hexathiophenes derivatives. The quenching experiments indicate that the scrambling is due to a "halogen dance" mechanism. In conclusion, the lack of scrambling is entirely consistent with the structural homogeneity of the poly(3-alkylthiophenes) 5, and their observed \(^1\)H and \(^{13}\)C NMR spectra.

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(21) For the sake of clarity in presentation, we have taken the liberty of naming our compounds with 3-alkyl group always remaining at position 3 and numbering other substituents accordingly.

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\[\text{Figure 3. Full } ^1\text{H and } ^{13}\text{C NMR of PHT prepared by the present method.}\]

**NMR Spectroscopy**

In 1990, Sato and Mori\(^{(11)}\) deduced through a series of two-dimensional \(^1\)H NMR studies that 54\% of electrochemically synthesized poly(3-dodecylthiophene) consisted of head-to-tail head-to-tail couplings. Therefore, almost half of the couplings in poly(3-alkylthiophenes) are defects with regard to the conducting polymer architecture. In their analysis, the four singlets in the aromatic region can be clearly attributed to the protons on the 4-position on the thiophene ring where each peak results from a different type of trimeric sequence of HT-HT (\(\delta = 6.98\)), HT-HH (\(\delta = 7.00\)), TT-HT (\(\delta = 7.02\)), and TT-HH (\(\delta = 7.05\)) linked thiophene rings. In contrast, our synthesis of PAT's afford strikingly clear \(^1\)H and \(^{13}\)C NMR spectra (Figure 3). As an example, Figures 3 and 4 show the full proton and carbon spectrum and the expanded aromatic and methylene regions of the \(^1\)H NMR spectra of poly(3-hexylthiophene) (PHT) as synthesized by this method. As a comparison the expanded \(^1\)H NMR for PHT as prepared by the FeCl\(_3\) method is shown in Figure 4. Figure 5 shows the \(^{13}\)C expanded aromatic region for our PHT. Both PHT's were prepared in our laboratory. The \(^1\)H and \(^{13}\)C NMR spectra,\(^{(11,22,23)}\) of a PHT as synthesized either electrochemically or chemically or by other methods have been published as part of other studies on the polymerization of dialkylthiophenes and related work and show a large number of imperfect couplings and random
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Figure 4. (a) Expanded $^1$H of PHT aromatic region prepared by this method. The inset shows the expanded $^1$H NMR of the PHT aryl methylene region. (b) Expanded $^1$H of PHT aromatic region prepared by the FeCl$_3$ method. The inset is the aryl methylene region. Both of these PHT samples are treated identically.

regiospecificity. The $^1$H and $^{13}$C NMR spectra show that our polymers contain almost exclusively head-to-tail couplings.

By analysis of the NMR data, our PHT contains approximately 98% HT-HT couplings, 1% HT-HH couplings, and 1% TT-HT couplings. A similar analysis indicates 93% of the desired regiochemistry in our PBT, 95% in PDDT, and 97% in POT. These data show that we have been able to gain regiocontrol over the polymerization reaction, which leads to essentially one structure.

The $^{13}$C NMR reinforces the interpretation of the $^1$H NMR data and shows the very high structural regularity in polymers prepared by this method. Figure 3 shows the full $^{13}$C spectrum for our poly(3-alkylthiophene). The alkyl region only shows six absorptions corresponding to the hexyl side chain at 14.9, 23.6, 29.8, 30.3, 30.9, and 32.0 ppm. Shown in Figure 5 is the expanded $^{13}$C aromatic region for PHT. The spectra for PHT and the entire PAT series show exclusively four predominant absorptions attributable to the carbons on one regiochemically defined thiophene ring. Absorptions at 128.5, 130.5, 134.0, and 140.0 represent the head-to-tail-coupled poly(3-hexylthiophene) structure. A $^{13}$C NMR of PHT made from FeCl$_3$, in addition to the HT-HT couplings, exhibits well-defined peaks at 125.2, 126.6, 127.4, 128.3, 129.6, 134.9, 135.7, 136.8, 140.3, 142.9, and 143.4 ppm. These absorptions represent the carbons associated with non-head-to-tail regiochemical isomers. Poly(3-hexylthiophene), prepared by our method, shows only very small absorptions at 127.4 and 126.7 and peaks barely distinguishable from the base line at 140.3 and 137.0, which correspond to the 1–2% of scrambling in the 2-bromo-3-alkyl-5-thiophene starting material. Based on these data and other literature $^{13}$C NMR data, we find no detectable head-to-tail-to-tail coupling in our alkylthiophene units.

These NMR results are in stark contrast to previously prepared materials.

Conformational Behavior of Oligomers of Alkylthiophenes

The effect of a microstructural irregularity is to create a sterically driven twist of the thiophene rings out of coplanarity and conjugation with one another. This is illustrated by the structural diagrams in Figure 6. The larger the torsion angle between thiophene rings, the greater the bandgaps will be in typical poly(3-alkylthiophenes) as compared to a structure with well-defined head-to-tail regiochemistry. Since the high electrical conductivity in the oxidized polymer results from the development of mid-gap bipolaron bands, the bandgap (and width) of the neutral polymer directly determines the electrical conductivity in these materials. It is currently accepted that the mechanism for conductivity in the polythiophenes, called the bipolaron mechanism, proceeds through a combination of a charge movement along the polymer chain (where charge carriers are bound dication) and through a polymer-to-polymer (and grain to grain) charge-hopping mechanism. The energetic costs of moving charge along a conjugated chain is directly related to the amount of molecular orbital overlap. It is, therefore, absolutely critical to have structurally homogeneous conducting polymers in order to allow for...
maximum intramolecular orbital overlap (large transfer integrals) as well as interchain stacking and overlap to reduce highly resistive charge transport pathways. Given that our poly(3-alkylthiophenes) have very few undesirable couplings, adjacent thiophene rings can now access a coplanar (or nearly coplanar) conformation of low energy.

In order to investigate the energetic consequences of ring coplanarity in poly(3-alkylthiophenes) with desirable HT couplings compared to the undesirable HH couplings, we have examined the conformations of model dimers, trimers, and tetramers of alkylthiophenes by both molecular mechanics and ab initio calculations. Results from the molecular mechanics calculations indicate that the lowest energy conformations for structures like A (Figure 6) have all the rings nearly coplanar. In contrast, structures like B have lowest energy conformations that possess a large twisting of the rings out of coplanarity at the HH junction (torsional angle between ring 7 and 8, in B). A detailed discussion of these results will appear in a forthcoming article; below we describe our preliminary findings.

Molecular mechanics performed on a 3-butylthiophene trimer with HT-HT coupling yield lowest energy conformations in which the thiophene rings are trans to each other and within 20° of coplanarity. The potential energy surface for twisting the rings from a coplanar conformation to ~20° out of coplanarity is very flat, the structures in this region are within <1 kcal of each other. We have also fully optimized the same trimer using ab initio methods at the STO-3G level. In a minimum energy structure for the HT-HT butyl trimer, the butyl groups are in a fully extended trans arrangement, the thiophenes are trans, and the torsional angles are both ~155°. In investigating the potential energy, the ab initio calculations mirror the molecular mechanics results by showing a fairly flat surface (<1 kcal), with structures having torsional angles of 180° to 130°.

Molecular mechanics on a HT-HH 3-butylthiophene show a minimum energy structure where the HT junction has a torsional angle of 175° and the HH junction has a torsional angle of 150°. A >±10° twist of the HH junction from 150° costs approximately 1 kcal, whereas a ±20° twist from 150° cost 5 kcal. We also calculated the structure of HT-HH 3-butylthiophene using ab initio methods at the STO-3G level. We have found two local minimum energy structures, each having a 155° torsional angle between the HT-coupled thiophene rings, and the HH torsional angles are 110° and 240°, respectively. By analyzing the potential energy surface, the torsional angle between the two thiophene rings can vary between 130° and 70° or between 230° and 260° at a cost of approximately 1 kcal/mol. We also explored moving the torsional angle closer to coplanarity. Structures with torsional angles near 140° or 220°, respectively, are 2.5 kcal/mol higher in energy. If the HH-coupled thiophenes rings have a torsional angle 10° closer to 180° (coplanarity), those structures are >5 kcal/mol higher in energy. Although these are gas-phase calculations and packing forces to a great extent determine the solid state structure, it is insightful to see that a head-to-head coupling, in a models for poly(3-alkylthiophenes), causes the torsional angles to be approximately 40° out of coplanarity. In contrast, a head-to-tail coupling can access very low energy structures that can possess coplanarity between alkylthiophene rings and lead to greater along the chain π overlap and small bandgaps.

Solution- and Solid-State Electronic Spectra

A qualitative measure of π orbital overlap can be observed in the electronic spectra of conjugated molecules. In conjugated polymers the extent of conjugation directly

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Table I. A Comparison of Solution- and Solid-State UV–vis Data of Poly(3-alkylthiophenes)

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* The thin film data is independent of the film thickness in the thickness regime of the films used in the measurement (3–10 μm). Cast from CHCl₃.

affects the observed energy of the π–π* transition, which appears as the maximum absorption in these materials. Experimental determination of the electronic spectra gives insight to the extent of conjugation and structure of PAT’s. The results of both the solid-state and solution UV–vis are shown below in Table I, and the solid-state spectra are shown in Figure 7. A number of interesting trends are observed by inspection. In the solution data, we observe for the first time a change in the λ<sub>max</sub> as a function of alkyl side chain. As indicated by lower energy shifts in the λ<sub>max</sub>, longer conjugation lengths are observed in the PAT’s possessing the longer alkyl side chains. Photoelectron spectroscopy and X-ray studies have indicated that PDDT possesses the longer alkyl side chains—the PAT’s containing these aggregates of two polymer chains in POT. This aggregation occurs at a great extent at low temperature and leads to a large thermochromic effect, marked by a deep red solution at 25 °C and a dark purple solution at ~40 °C.

The shift to lower energy of the λ<sub>max</sub> in PDDT prepared by our method is found to be 14 nm (450 nm) in solution, 46 nm (526 nm) in the solid state, and other intense lower energy peaks with shifts of up to 129 nm (609 nm) relative to PDDT prepared with FeCl₃. We interpret this effect as an increasing steric interaction between longer alkyl chains found in the FeCl₃ samples—these PAT’s contain undesirable couplings. As noted in Figure 6 in structure B, sterically repulsions between the alkyl chain on the thiophene ring 6 and the alkyl chain on thiophene 8 will be a maximum when the alkyl chain is the longest, thereby decreasing conjugation between thiophene rings.

Figure 7. UV–vis of these PAT’s in the solid state. Labeled absorbances are the λ<sub>max</sub> and fine structure peaks. Label at 675 nm is a marker near the band edge (~1.8 eV).

Accordingly, the largest Δλ<sub>max</sub> should occur in the PAT’s with longest alkyl chains. Molecular modeling studies indicate that butyl side chains are long enough to sterically interfere, and therefore increase steric interactions should occur with the longer side chains.

A direct comparison of our data with data on highly ordered, very thin films of poly(3-methylthiophene) gives insight on the macroscopic order in PAT films reported here. The highest value for the electrical conductivity for a PAT is 2000 S cm⁻¹ and was observed in 0.2-μm thick films of poly(3-methylthiophene) (PMT), which had a λ<sub>max</sub> of 510 nm. These highly conducting PMT films exhibited...
thickness-dependent solid-state UV-vis spectra, which correlated with the conjugation lengths and electrical conductivity. The thinnest films in which conductivity measurements were reported were 0.19 μm, although λmax values as high 552 nm were observed in the 0.006–μm films. These thin films of PMT had a very high degree of structural order and extended π-conjugation lengths. In much thicker films (3–10 μm) of our PAT’s, we find that the λmax of POT is 520 nm and PDDT is 526 nm. We observe conjugation lengths of the order of very highly ordered poly(3-methylthiophene). These results indicate that the packing arrangements and molecular structures these PAT’s are ordered at a comparable level to ultrathin films of poly(3-methylthiophene). In addition, X-ray studies on thin films of our PAT’s (in our laboratory) have shown highly ordered structures which are more oriented than stretch-oriented PAT’s (from the FeCl3 method). This type of behavior has also been observed for oligomers of thiophene.38 We expect that this relative intensity ratio is an indication of the amount of highly ordered phases present in the solid-state thin films.

Conclusion

We have presented a synthetic methodology that produces structurally homogeneous poly(3-alkylthiophenes). Due to their structural homogeneity, these materials give a clearer picture of structure–property relationships in conjugated polymers. The ability to acquire data which are unobscured by structurally defective materials is crucial in defining the chemistry and physics of conducting organic materials and the systematic of their nonlinear optical behavior. We believe that the synthesis of well-defined materials is the first step toward the design and engineering of conjugated π architectures that will self-assemble in three dimensions and possess exceptional electronic and optical properties.

Experimental Section

All reactions were performed under prepurified nitrogen or argon, using dry glassware. Glassware was either dried in an oven overnight or flame dried and then cooled under a stream of argon or nitrogen. Tetrahydrofuran and diethyl ether were dried over Na benzophenone ketyl radical and freshly distilled prior to use. Trimethylalyl chloride was freshly distilled prior to use. Disopropylamine was dried over CaH2 and distilled prior to use. Acetic acid was used as received. All 2-bromo-3-alkylthiophenes were freshly distilled prior to use. Both MgBr2·OEt2 and Ni(dppe)Cl2 were purchased from the Aldrich Chemical Co. and were used as received and were ideally stored in a drybox.

H and 13C NMR spectra were recorded on an IBM Bruker FT300 spectrometer. All 300-MHz 1H NMR spectra were recorded in CDCl3 and are reported in ppm as δ relative internal tetramethylsilane at 0.0 ppm. The amount of head-to-tail coupling was determined by NMR integration of the small peaks near 7.0 using the Sato and Morii analysis and the peaks near 5.25 using the method of Eisenbeuemer et al. Both methods gave consistent results. The integrated numbers of protons for the regiochemical isomers other than the head-to-tail (HT-HT) ones in the 1H NMR spectra is given relative to the integrated area of the 4-proton on the major isomer. For example, 2% of a HT-HH polymer will be listed as 7.04 (a, 0.02 H), where the HT-HT polymer is 7.00 (a, 1 H). All 75.4 MHz 13C NMR were taken in CDCl3 and are reported relative to internal, residual CHCl3 at 77.0 ppm. All UV-vis spectra were taken on either polymer solutions in CHCl3 or polymer thin films cast onto quartz cuvettes using a Hewlett-Packard 8451A diode-array spectrophotometer and are reported in λ and are in nm. Infrared spectra were obtained on polymer thin films cast from CHCl3 onto NaCl plates using a Nicolet 7199 FTIR and are reported in cm−1. All 3-alkylthiophenes and 2-bromo-3-alkylthiophenes were purified by vacuum fractional distillation and were characterized by 1H NMR, GC/MS, and elemental analysis. Gas chromatography/mass spectroscopy was performed on a Hewlett-Packard 59970 GC/MS workstation. The GC column was a Hewlett-Packard fused silica capillary column cross-linked with 5% phenyl methyl silicone. Elemental analysis was performed using Midwest MicroLab, Indianapolis, IN. All molecular mechanics calculations were performed using Charmm software (Polygen, Inc.) on a Silicon Graphics Iris 4D Computer. The 3-butyliophene trimer structures were optimized at the ab initio Hartree–Fock STO-3G level using Gaussian 92.

Preparation of 3-n-Alkylthiophenes 3a–d. All 3-alkylthiophenes were prepared by the literature procedure of Kumada using the specific synthetic details outlined by Zimmer et al.46 All compounds were purified by distillation and purity checked and structures characterized by 1H NMR and GC/MS. All are literature compounds. Zimmer has synthesized and reported data for 3-butyliophene and 3-hexyliophene.

3-n-Octylthiophene (3e). The crude product obtained from 12.7 g (78 mmol) of 3-bromothiophene was distilled (79 °C (0.35 mmHg)) to give 9.4 g (61%) of the product: 1H NMR (CDCl3) 7.23 (dd, J = 4.5 Hz, 1 H), 6.93 (m, 2 H), 2.62 (m, 2 H), 1.63 (m, 2 H), 1.38–1.20 (m, 10 H), 0.88 (t, J = 5.7 Hz); MS m/z (relative intensity) 196 (16, M+), 97 (100, C6H10S+). Purity was determined to be >99% pure by GC.

3-n-Dodecylthiophene (3d). The crude product obtained from 16.3 g (100 mmol) of 3-bromothiophene was distilled (175 °C (1.8 mmHg)) to give 18.3 g (73%) of the product: 1H NMR (CDCl3) 7.17 (dd, J = 2.4 Hz, 2 H), 6.86 (m, 2 H), 2.02 (m, 2 H), 1.7 (t, J = 7 Hz, 2 H), 1.61 (m, 2 H), 1.3–1.2 (m, 18 H), 0.86 (t, J = 6 Hz);


Table II. Fine Structure in Solid-State UV–vis Data of Structurally Homogeneous Poly(3-alkylthiophenes)

<table>
<thead>
<tr>
<th>Structure</th>
<th>λmax (FeCl3)</th>
<th>λmax-rel intensity (our method)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PBT</td>
<td>480a</td>
<td>500a</td>
</tr>
<tr>
<td></td>
<td>590</td>
<td>580</td>
</tr>
<tr>
<td></td>
<td>610</td>
<td></td>
</tr>
<tr>
<td>PHT</td>
<td>480b</td>
<td>504–2.2</td>
</tr>
<tr>
<td></td>
<td>550–1.8</td>
<td></td>
</tr>
<tr>
<td></td>
<td>600–1.0</td>
<td></td>
</tr>
<tr>
<td>POT</td>
<td>480b</td>
<td>520–1.6</td>
</tr>
<tr>
<td></td>
<td>553–1.6</td>
<td></td>
</tr>
<tr>
<td></td>
<td>603–1.0</td>
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</tr>
<tr>
<td>PDDT</td>
<td>480b</td>
<td>526–1.8</td>
</tr>
<tr>
<td></td>
<td>561–1.6</td>
<td></td>
</tr>
<tr>
<td></td>
<td>609–1.0</td>
<td></td>
</tr>
</tbody>
</table>

Structurally Homogeneous Poly(3-alkythiophenes)

MS m/z (relative intensity) 252 (10, M⁺), 97 (100, C₈H₇S+). Purity was determined to be >96% pure by GC.

Preparation of 2-Bromo-3-n-alkylthiophenes (4a-d). All 2-bromo-3-alkylthiophenes were prepared according to Gronowitcz et al. The boiling point and NMR characterization of 2-bromo-3-hexythiophene has been reported.

2-Bromo-3-n-butylthiophene (4a). Into a dry round-bottom flask was placed 68.5 mL (0.5 M) of acetic acid, which was then sparged with argon (5 min). Then 7.7 g (0.055 mol) of freshly distilled 3-n-butylthiophene (3a) was added. The mixture was cooled to 10 °C, whereupon a 2.5 M solution of bromine (2.8 mL, 0.055 mol) in acetic acid was added dropwise from an addition funnel over a period of 30 min, while the temperature was maintained at 10-15 °C. The material was then stirred in an ice bath for 30 min and was then poured onto ice. The mixture was then aspirated through a CH₂Cl₂, the CH₂Cl₂ layer washed with NaOH until pH ~ 6 and dried over MgSO₄, and the solvent removed by rotary evaporation. The product was twice distilled (80 °C (1.8 mmHg)) to yield 5.8 g (48%) of 4a: 1H (CDCl₃) 7.11 (d, J = 5.7 Hz, 1 H), 6.72 (d, J = 5.7 Hz, 1 H), 2.50 (t, J = 7.4 Hz, 2 H), 1.49 (pentet, J = 7.1 Hz, 2 H), 1.22 (sextet, J = 7.1 Hz), 0.86 (t, J = 7.5 Hz); MS m/z (relative intensity) 220 (17.5, M⁺), 137 (13, M⁺ - HBr), 97 (100, C₈H₇S⁺). Anal. Calcd for C₈H₁₅BrS: C, 48.59; H, 6.12; Br, 32.32; S, 12.97. % yield.

Preparation of Poly(3-octylthiophene) Using 2 × 0.5 mol % Catalyst. The exact procedure was performed as listed in the preparation of PHT above except on a 1.8 mmol scale; however, after stirring for 15 h, 0.41 mol % of Ni(dppp)Cl₂ was added (40 mg, 0.074 mmol) at 25 °C. The solution was then stirred an additional 18 h. The polymer was then precipitated with MeOH (400 mL) and allowed to sit for 2 days in MeOH, and the red precipitate was allowed to settle. The solution was decanted and the solid filtered and washed with MeOH, H₂O, and MeOH again. The solid was dried under vacuum and Soxhlet extracted with MeOH and hexanes. The polymer was then dissolved in CH₂Cl₂ using a Soxhlet extractor, the CH₂Cl₂ was removed, and the residue was dried and yield was 2.28 g of 96% head-to-tail coupled poly(3-octylthiophene) (65% yield). The most recent preparation gave 97% HT-HT-coupled PHT: 1H NMR (CDCl₃) 6.98 (s, 1 H), 2.78 (t, 2 H), 1.62 (q, 2 H), 1.48 (m, 2 H), 1.36 (m, 4 H), 0.90 (t, 3 H); peaks also present that are representative of 5% of other regiochemical isomers are assigned at 7.04 (s, 0.01 H), 7.00 (s, 0.04 H), 2.60 (m, 0.04 H); 13C NMR (1H decoupled) 140.0, 134.0, 130.5, 128.5, 31.8, 30.5, 29.5, 29.3, 28.5, 14.0; relative intensities are coupled to relaxation times; however, the relative intensity of observable small peaks (relative to the 128.5 absorption) are 127.4 (0.05), 126.7 (0.02), 140.3 (0.01), 139.8 (0.01); UV-vis (CDCl₃) (λmax, nm, ε, cm⁻¹): 444 (13, 15 000), 344 (10, 16 500), (Film, cast from CHCl₃) λ (relative intensity), 504 nm (2.2), 550 nm (1.8), 600 nm (1.0), band edge 660 nm (1.9 eV). GPC analysis of the THF-soluble solid polymer indicates an average molecular weight (Mₐ) of around 10 000, with a polydispersity of 1.6. A Cs₂SO₄-soluble fraction (insoluble in CHCl₃ and THF) is a HT-HT-coupled PHT with an identical 1H NMR to the CHCl₃-soluble polymer and is thought to be a polymer of higher molecular weight.

Preparation of Poly(3-octylthiophene) Using 2 × 0.5 mol % Catalyst. The exact procedure was performed as listed in the preparation of PHT above except on a 1.8 mmol scale; however, after stirring for 15 h, 0.41 mol % of Ni(dppp)Cl₂ was added (40 mg, 0.074 mmol) at 25 °C. The solution was then stirred an additional 18 h. The polymer was then precipitated with MeOH (400 mL) and allowed to sit for 2 days in MeOH, and the red precipitate was allowed to settle. The solution was decanted and the solid filtered and washed with MeOH, H₂O, and MeOH again. The solid was dried under vacuum and Soxhlet extracted with MeOH and hexanes. The polymer was then dissolved in CH₂Cl₂ using a Soxhlet extractor, the CH₂Cl₂ was removed, and the residue was dried and yield was 2.28 g of 96% head-to-tail coupled poly(3-octylthiophene) (65% yield). The most recent preparation gave 97% HT-HT-coupled PHT: 1H NMR (CDCl₃) 6.98 (s, 1 H), 2.72 (t, 2 H), 1.63 (m, 2 H), 1.22 (m, 10 H), 0.81 (m, 3 H), peaks also appear that represent 4% of other regiochemical isomers are assigned at 7.06 (s, 0.04 H), 6.97 (s, 0.001 H), 2.6 (m, 0.01 H); 13C NMR (1H decoupled) 140.0, 133.8, 130.6, 128.5, 31.9, 30.6, 29.3, 29.0, 23.0, 14.2; the relative intensity of the small absorptions (relative to the 128.5 absorption) are 127.2 (0.08), 126.6 (0.03), 139.8 (0.01), 127.2 (0.01); UV-vis (CDCl₃) (λmax, nm, ε, cm⁻¹): 444 (13, 15 000), band edge 660 nm (1.9 eV). GPC analysis of the THF-soluble solid polymer indicates an average molecular weight (Mₐ) of around 24, 424 with a polydispersity of 1.98.

A Representative Quenching Reaction: Reaction of 2-Bromo-3-bromo-2-nBuLi with LDA, Followed by Quenching with TMSCl. 2-Bromo-3-butyl-5-(trimethylisilyl)thiophene. The quenching studies were performed on a 1.5 mmol scale, and the 2-bromo-3-butyl-5-lithiothiophene was generated in the quenching studies identical to those described below. After generation of the 2-bromo-3-butyl-5-lithiothiophene, an excess of TMSCl was added at ~60 °C and the reaction allowed to warm to room temperature overnight (~12 h). The reaction mixture was then poured onto water, the products were extracted into...
Et₂O, dried over MgSO₄, filtered, and the solvent was removed in vacuo to recover 99% of 2-bromo-3-butyl-5-(trimethylsilyl)-thiophene (¹H NMR 6.91 ppm, GC tᵣ = 12.42 min) and 1% of 2-(trimethylsilyl)-3-butyl-5-bromothiophene (6.95 ppm, GC tᵣ = 13.02 min) as determined by ¹H NMR and GC/MS. Assignments are based on ¹H NMR of similar compounds prepared in our laboratory. Quenching studies on both the 5-lithium and 5-magnesium bromide of 2-bromo-3-dodecylthiophene were performed under identical conditions. In preparation of the Grignard species, we allowed the reaction mixture containing the 5-lithiospecies and MgBr₂·Et₂O to warm to room temperature before quenching with TMSCl.

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Supplementary Material Available: ¹H and ¹³C NMR spectra of poly(3-hexylthiophene) prepared from the FeCl₃ method and 5a, 5c, and 5d (both full and expanded) (14 pages). This material is contained in 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.