

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

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The full details of a facile synthesis of *structurally homogeneous* poly(3-alkylthiophenes) (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-alkylthiophenes) 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 conducting organic polymers, chemists have sought to prepare polymers that both are soluble (and/or processable) and exhibit high electrical conductivities.¹ Such an advancement must be made if conducting polymers² are to fulfill their promise as materials for molecular electronic devices. The early problems concerning material intractability have been thoroughly addressed,³ 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 structure⁴ of a given material and thereby determine its electrical⁵ and optical properties.⁶ Molecular engineering must begin with the synthesis of homogeneous

structures.^{7,8} 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 Naarman polyacetylene.⁷ Classical synthetic methods produce defective polyacetylene with sp³-hybridized defects at junctions of cross-links between polymer chains.⁹ Given that the degree of π overlap along the chain directly determines the band widths (and gap) and sp³ centers decrease the conjugation, classically prepared polyacetylenes will possess larger band gaps than a more structurally homogeneous material. Indeed, a number of theoretical studies have shown that coplanarity along the chain π orbitals leads to better electrical properties^{5c,d} and nonlinear optical properties.⁶ As one example, Naarman's defect-free polyacetylene exhibits electrical conductivities close to that of copper,⁷ in the I₂-doped material, and is expected to exhibit large third-order susceptibilities.⁶ It is clear that the ability to design and control conjugated π architectures is the key to creating new advanced materials, and some elegant examples have recently appeared in the literature.^{8,10}

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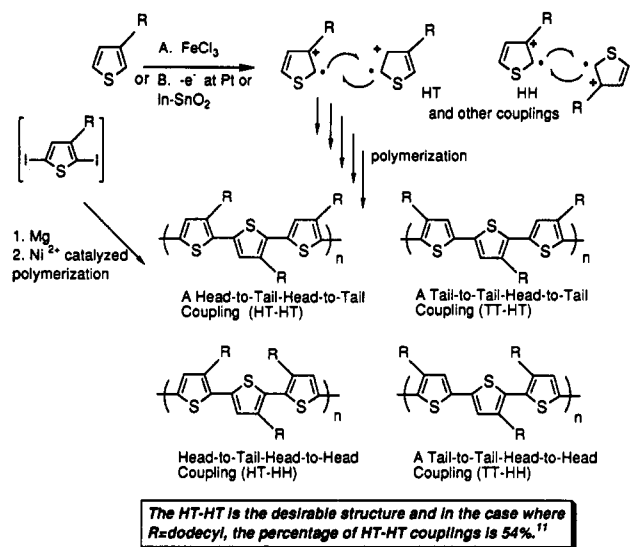


Figure 1.

Poly(3-alkylthiophenes) represent a class of conducting polymers that are soluble and processable and yet retain the magnitude of electrical conductivity of the insoluble parent, polythiophene. Similar to classical polyacetylene, the standard synthetic methods (Figure 1) used to make PAT's generate a large number of defects due to the random couplings¹¹ at the 2,5 positions on the thiophene ring. The resultant structures must contain large numbers of thiophene rings that are twisted far out of conjugation due to steric interactions between alkyl chains (a detailed reasoning is given in electronic spectra section). A structurally homogeneous head-to-tail (HT) arrangement would therefore improve the material's electronic and optical properties.¹² A synthesis of this regiochemical arrangement requires a synthetic method that give absolute regiocontrol at each coupling step in the polymerization reaction.

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).^{10e} 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

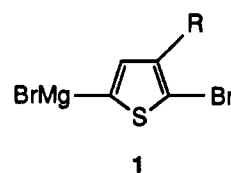
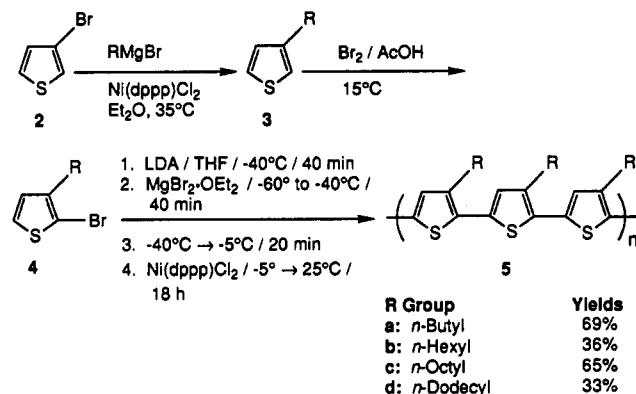


Figure 2.

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



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^{10e} 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-coupling¹³ target compounds such as 1 (Figure 2). The synthesis that leads to structurally homogeneous poly(3-alkylthiophenes) is shown in Scheme I. The 3-alkylthiophenes (3) were prepared in 60–80% yields.¹⁴ Contrary to the regiospecific 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.¹⁵ 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-lithiothiophene with magnesium bromide etherate to afford 1. Subsequent treatment of 1, in situ with Ni(dppp)Cl₂,^{14,16} leads to regiochemically defined head-to-tail-coupled poly(3-alkylthiophenes).

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(12) Results by Elsenbaumer have shown that the polymerization of a 3-butylthiophene-3-methylthiophene dimer which contains a 63:37 mixture of a HT-HH couplings leads to a 3-fold increase in electrical conductivity over the random copolymerization reaction; see: Elsenbaumer, R. L.; Jen, K.-Y.; Miller, G. G.; Eckhardt, H.; Shacklette, L. W.; Jow, R. *Electronic Properties of Conjugated Polymers*; Kuzmany, H., Mehring, M., Roth, S., Eds.; Springer Series in Solid State Sciences 1987, 76, 400.

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-position¹⁸ both regioselectively and without extensive scrambling of the generated organolithium. In previous studies on thienyllithium species, we and others have found that regioselective metalation of bromothiophenes¹⁹ 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-lithiothiophene²¹ 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-bromothiophene 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** → **5**) provides <1–3% of scrambled product. In the case of R = *n*-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 ¹H 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-hexylthiophene 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 ¹H and ¹³C 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.

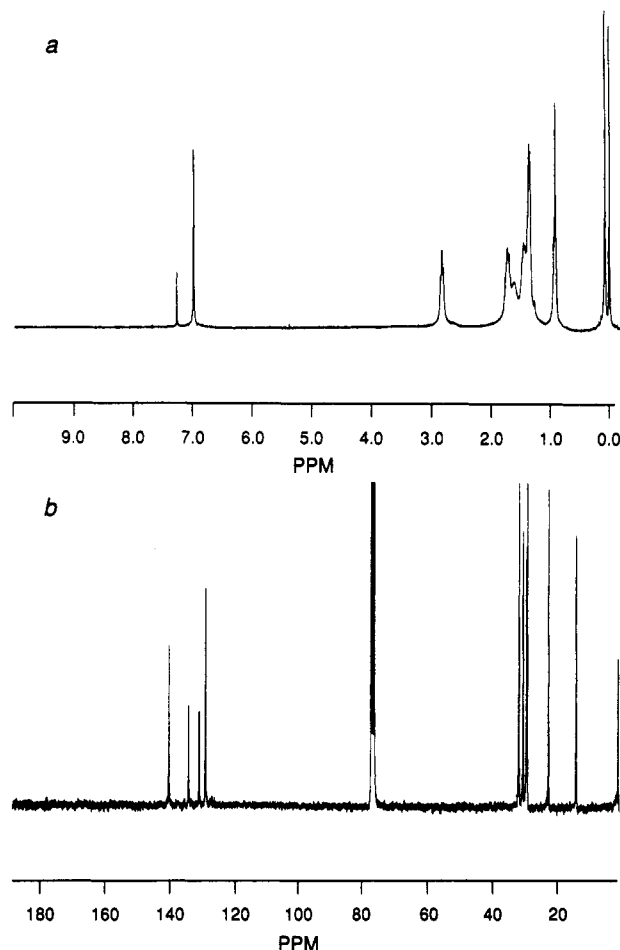


Figure 3. Full ¹H and ¹³C NMR of PHT prepared by the present method.

NMR Spectroscopy

In 1990, Sato and Morii¹¹ deduced through a series of two-dimensional ¹H 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 (δ = 6.98), HT-HH (δ = 7.00), TT-HT (δ = 7.02), and TT-HH (δ = 7.05) linked thiophene rings. In contrast, our synthesis of PAT's afford strikingly clear ¹H and ¹³C 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 ¹H NMR spectra of poly(3-hexylthiophene) (PHT) as synthesized by this method. As a comparison the expanded ¹H NMR for PHT as prepared by the FeCl₃ method is shown in Figure 4. Figure 5 shows the ¹³C expanded aromatic region for our PHT. Both PHT's were prepared in our laboratory. The ¹H and ¹³C NMR spectra,^{11,22,23} of a PAT as synthesized either electrochemically or chemically or by other methods have been published as part of other studies on the polymerization of dialkylbithiophenes and related work and show a large number of imperfect couplings and random

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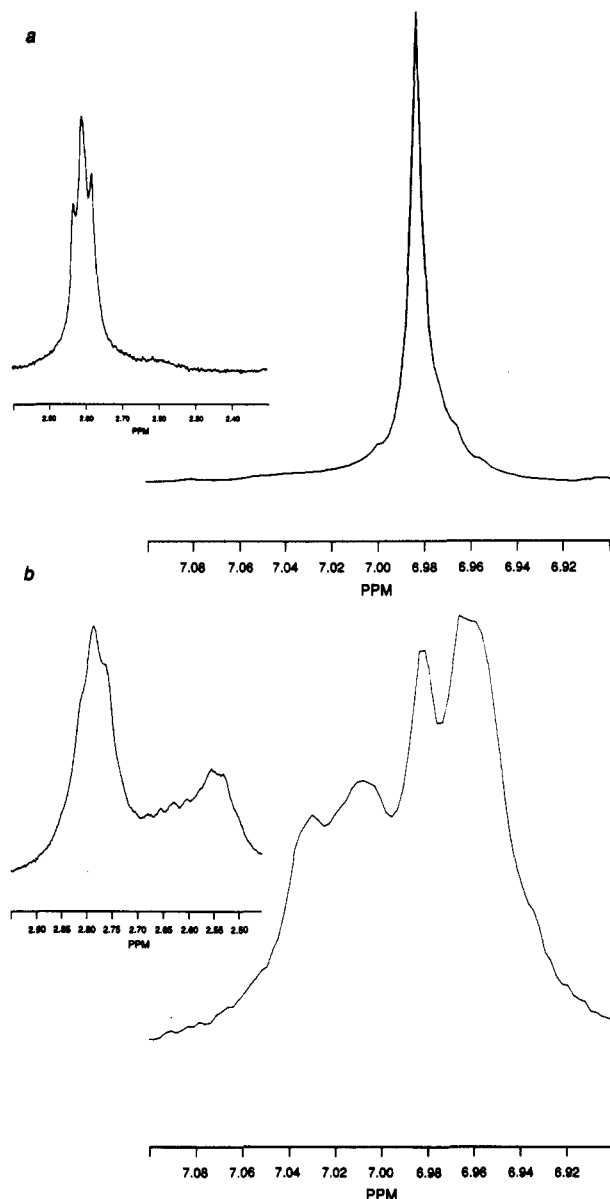


Figure 4. (a) Expanded ^1H of PHT aromatic region prepared by this method. The inset shows the expanded ^1H NMR of the PHT aryl methylene region. (b) Expanded ^1H NMR of PHT aromatic region prepared by the FeCl_3 method. The inset is the aryl methylene region. Both of these PHT samples are treated identically.

regiospecificity. The ^1H and ^{13}C NMR spectra show that our polymers carry 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 ^1H 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-hexylthiophene). 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.²³ 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-lithiothiophene starting material. Based on these data and other literature ^{13}C NMR data,^{23a} we find no detectable head-to-head-tail-to-tail coupling in our alkylthiophene units.²⁴ 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,^{5a} 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^{25,26} (where charge carriers are bound dications) and through a polymer-to-polymer (and grain to grain) charge-hopping mechanism.²⁷ 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

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(24) Since very small amounts of monomers possess the regiochemistry that would lead to non-head-to-tail coupling, the probability of two "bad" couplings occurring in a row is remote.

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(27) Jeon, D.; Kim, J.; Gallagher, M. C.; Willis, R. F. *Science (Washington, D.C.)* 1992, 256, 1662.

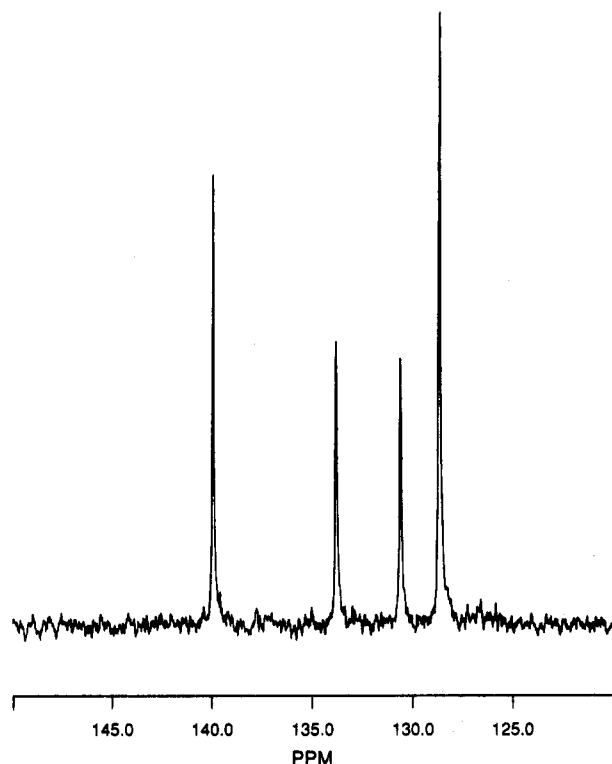


Figure 5. Expanded ^{13}C NMR of PHT aromatic region prepared by this method.

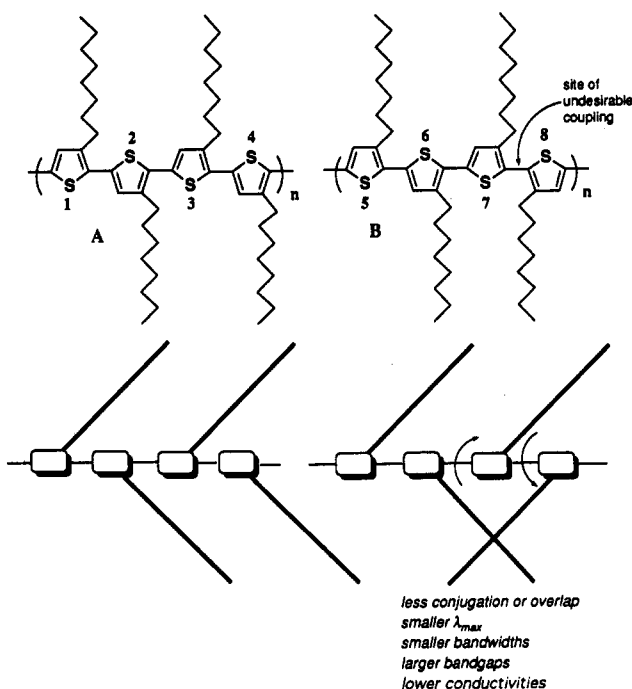


Figure 6.

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 mo-

lecular mechanics and ab initio calculations.^{5d,28} 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.²⁹

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 $\sim 20^\circ$ 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 $\sim 155^\circ$. 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 structures where the HT junction has a torsional angle of 175° and the HH junction has a torsional angle of 150° . A $\pm 10^\circ$ twist of the HH junction from 150° costs approximately 1 kcal, whereas a $\pm 20^\circ$ 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)

| structure | soln λ_{\max} (FeCl ₃)* | soln λ_{\max} (this method) | solid-state λ_{\max} (FeCl ₃)* | solid-state ^a λ_{\max} (this method) |
|-----------|---|---|--|---|
| PBT | 436 | 438 | 480 | 500 |
| PHT | 436 | 442 | 480 | 504 |
| POT | 436 | 446 | 480 | 520 |
| PDDT | 436 | 450 | 480 | 526 |

^a 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_{\max} as a function of alkyl side chain. As indicated by lower energy shifts in the λ_{\max} , 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 is more planar and stacked (lamellar-like)³⁰ in structure and PBT is probably more helical³¹ in nature. The solution UV-vis data presented here corroborate a helical structure for PBT and a lamellar structure for PDDT. X-ray studies by Winokur and co-workers have further established the lamellar-like structure in PAT's with longer side chains in the solid state.³² It would appear that even in solution an aggregation of the alkyl side chain occurs in PDDT giving rise to greater conjugation lengths versus that of PBT. Preliminary light scattering in solution³³ results show such aggregation of two polymer chains in POT. This aggregation occurs to a great extent at low temperature and leads to a large thermochromic effect,³⁴ 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_{\max} 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 is found in the FeCl₃ samples—these PAT's contain undesirable couplings. As noted in Figure 6 in structure B, steric repulsions between the alkyl chain on the thiophene ring 6 and the alkyl chain on thiophene 8 will be at a maximum when the alkyl chain is the longest, thereby decreasing conjugation between thiophene rings.

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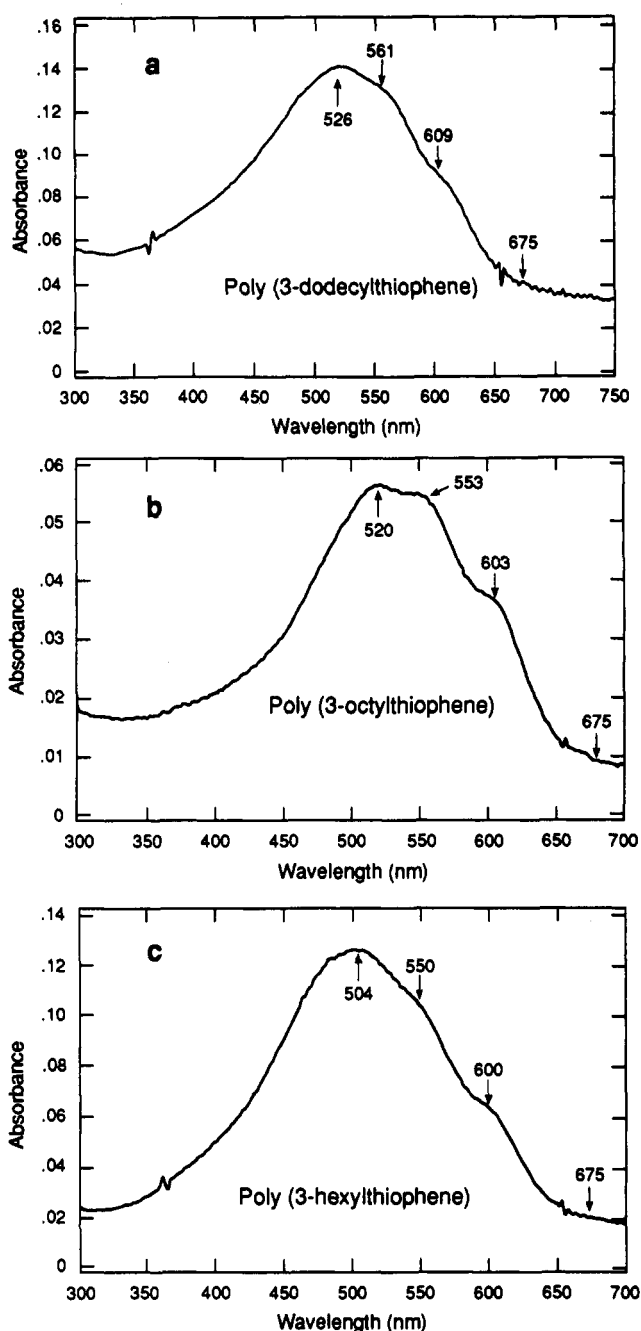


Figure 7. UV-vis of these PAT's in the solid state. Labeled absorbances are the λ_{\max} and fine structure peaks. Label at 675 nm is a marker near the band edge (≈ 1.8 eV).

Accordingly, the largest $\Delta\lambda_{\max}$ ³⁵ 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)³⁶ 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 thin films of poly(3-methylthiophene) (PMT), which had a λ_{\max} of 510 nm. These highly conducting PMT films exhibited

(35) $\Delta\lambda_{\max} = |(\lambda_{\max}(\text{PAT by our method}) - \lambda_{\max}(\text{PAT by FeCl}_3 \text{ method}))|$.

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

| structure | solid-state λ_{\max} (FeCl ₃) ^a | solid-state λ_{\max} -rel intensity (our method) |
|-----------|--|--|
| PBT | 480 ^a 590 | 500 ^a 580 610 |
| PHT | 480 ^b | 504 ^c -2.2 550-1.8 600-1.0 |
| POT | 480 ^b | 520 ^c -1.6 553-1.6 603-1.0 |
| PDDT | 480 ^b | 526 ^c -1.8 561-1.6 609-1.0 |

^a Broad absorbance exhibiting barely discernable shoulders; relative intensity of absorbances were not determined. Relative intensity is a measure of the absorbance relative to the smallest peak reported. ^b Broad absorbance with no discernable shoulders. ^c Broad absorbance with well-defined shoulders.

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 λ_{\max} 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 λ_{\max} 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).³⁷

In the solid-state data, we have also observed a series of well-defined long wavelength shoulders in the UV-vis data for the structurally homogeneous PAT's (Figure 7 and Table II). Our interpretation is that additional long-range ordered structures exist that give rise to longer conjugation lengths. The "shoulder" peaks present are quite substantial as indicated by the relative intensities of the "shoulder" to the λ_{\max} . 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 systematics 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. Trimethylsilyl chloride was freshly distilled prior to use. Diisopropylamine 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(dppp)Cl₂ were purchased from the Aldrich Chemical Co. and were used as received and were ideally stored in a drybox.

¹H 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 to 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 2.5 using the method of Elsenbaumer et al.¹² 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 (s, 0.02 H), where the HT-HT polymer is 7.00 (s, 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 ν as 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 by Midwest Microlab, Indianapolis, IN. All molecular mechanics calculations were performed using Charmm software (Polygen, Inc.) on a Silicon Graphics Iris 4D Computer. The 3-butylthiophene trimer structures were optimized at the ab initio Hartree-Fock STO-3G level using Gaussian 92.³⁹

Preparation of 3-*n*-Alkylthiophenes 3a-d. All 3-alkylthiophenes were prepared by the literature procedure of Kumada^{14a} using the specific synthetic details outlined by Zimmer et al.^{14b} All compounds were purified by distillation and purities checked and structures characterized by ¹H NMR and GC/MS. All are literature compounds. Zimmer has synthesized and reported data for 3-butylthiophene and 3-hexylthiophene.

3-*n*-Octylthiophene (3c). 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 (t, *J* = 7.5 Hz, 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, C₈H₅S⁺). 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, 4.0 Hz, 1 H), 6.86 (m, 2 H), 2.54 (t, *J* = 7 Hz, 2 H), 1.61 (m, 2 H), 1.3–1.2 (m, 18 H), 0.86 (t, *J* = 6 Hz);

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MS m/z (relative intensity) 252 (10, M^+), 97 (100, $C_5H_5S^+$). Purity was determined to be >99% pure by GC.

Preparation of 2-Bromo-3-*n*-alkylthiophenes 4a–d. All 2-bromo-3-alkylthiophenes were prepared according to Gronowitz et al.¹⁵ The boiling point and NMR characterization of 2-bromo-3-hexylthiophene has been reported.¹⁵

2-Bromo-3-*n*-butylthiophene (4a). Into a dry round-bottom flask was placed 68.5 mL (0.8 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 extracted into $CHCl_3$, the $CHCl_3$ layer washed with NaOH until pH ~6 and dried over $MgSO_4$, 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 NMR ($CDCl_3$) 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, $M + 2$), 218 (18, M^+), 97 (100, $C_5H_5S^+$). Anal. Calcd for $C_8H_{11}BrS$: C, 43.85; H, 5.06. Found: C, 43.72; H, 5.12. Purity was also checked by GC/MS.

2-Bromo-3-*n*-hexylthiophene (4b). Compound 4b was prepared in an identical fashion as 4a, except that the crude product was isolated by extraction with Et_2O . The crude product was obtained from a reaction starting with 20.6 g (83 mmol) of 3b. The product was distilled (117 °C (3.8 mmHg)) to give 10.0 g (49%) of 4b: 1H NMR ($CDCl_3$) 7.18 (d, J = 5.5 Hz, 1 H), 6.79 (d, J = 5.5 Hz, 1 H), 2.62 (t, J = 7.5 Hz, 2 H), 1.62–1.52 (m, 2 H), 1.35–1.23 (m, 6 H), 0.89 (t, J = 5 Hz, 3 H); MS m/z (relative intensity) 248 (56, $M + 2$), 246 (57, M^+), 97 (100, $C_5H_5S^+$). Anal. Calcd for $C_{10}H_{13}BrS$: C, 48.59; H, 6.12; Br, 32.32; S, 12.97. Found: C, 48.70; H, 6.17; Br, 32.16; S, 12.99. Purity was also checked by GC/MS.

2-Bromo-3-*n*-octylthiophene (4c). Compound 4c was prepared in an identical fashion as 4b. The crude product was obtained from reaction starting with 17.07 g (87 mmol) of 3c. The product was distilled (123 °C (1.1 mmHg)) to give 9.4 g (40%) of 4c: 1H NMR ($CDCl_3$) 7.18 (d, J = 5.7 Hz, 1 H), 6.79 (d, J = 5.7 Hz, 1 H), 2.56 (t, J = 7.5 Hz, 2 H), 1.58–1.50 (m, 2 H), 1.34–1.21 (m, 10 H), 0.89 (t, J = 4.5 Hz, 3 H); MS m/z (relative intensity) 276 (12, $M + 2$), 274 (13, M^+), 97 (100, $C_5H_5S^+$). Anal. Calcd for $C_{12}H_{15}BrS$: C, 52.36; H, 6.96. Found: C, 52.43; H, 7.09. Purity was also checked by GC/MS.

2-Bromo-3-*n*-dodecylthiophene (4d). Compound 4d was prepared in an identical fashion as 4b. A preparation of 4d from 9.4 g (0.037 mol) of freshly distilled 3-dodecylthiophene yielded after distillation (165 °C (0.22 mmHg)) 5.0 g (41%) of product: 1H NMR ($CDCl_3$) 7.19 (d, J = 5.3 Hz, 1 H), 6.79 (d, J = 5.3 Hz, 1 H), 2.58 (t, J = 7.5 Hz, 2 H), 1.64–1.57 (m, 2 H), 1.36–1.20 (m, 18 H), 0.88 (t, J = 5.0 Hz, 3 H); MS m/z (relative intensity) 332 (3, M^+), 97 (100, $C_5H_5S^+$). Anal. Calcd for $C_{16}H_{21}BrS$: C, 58.00; H, 8.21. Found: C, 58.20; H, 8.25. Purity was also checked by GC/MS.

General Synthesis of Poly(3-alkylthiophenes) (PAT). All PAT's were prepared in procedures identical to the procedure below. In some cases, after the addition of 0.5 mol % of $Ni(dppp)Cl_2$ and stirring for approximately 12 h, another 0.5% of $Ni(dppp)Cl_2$ was added. In the case of POT, a double addition of the catalyst resulted in an increase in yield to 65% from 36% and an average molecular weight increase from $M_w \approx 12\,000$ to $M_w \approx 24\,000$ (by GPC). We have also precipitated the PAT into hexane instead of methanol with no apparent changes in yield or purity. Example preparations are given below.

Preparation of Poly(3-hexylthiophene) Using 0.5 mol % Catalyst. Into a dry round-bottom flask was placed dry diisopropylamine (2.11 mL, 15 mmol) and freshly distilled, dry THF (75 mL, 0.2 M). To the mixture was added 6.0 mL of 2.5 M *n*-butyllithium (15 mmol) at room temperature. The mixture was cooled to –40 °C and stirred for 40 min. The reaction mixture containing LDA was then cooled to –78 °C, and 2-bromo-3-hexylthiophene (3.7 g, 15 mmol) was added. The mixture was stirred for 40 min at –40 °C. The mixture was then cooled to –60

°C, $MgBr_2 \cdot Et_2O^{40}$ (3.87 g, 15 mmol) was added, and the reaction was stirred at –60 °C for 20 min. The reaction was then warmed to –40 °C and stirred for 15 min. The reaction was then allowed to slowly warm to –5 °C, whereupon all of the $MgBr_2 \cdot Et_2O$ had reacted. At –5 °C, 0.48 mol % of $Ni(dppp)Cl_2$ (39 mg, 0.072 mmol) was added. The mixture was allowed to warm to room temperature overnight (~12–18 h). The polymer was then precipitated with MeOH (300 mL), and the resulting red precipitate was then filtered and washed with MeOH, H_2O , and MeOH again. The solid was then dried under vacuum. Removal of oligomers and impurities was achieved by subjecting the solid to Soxhlet extractions with MeOH first followed by hexanes. The polymer was then dissolved in $CHCl_3$ using a Soxhlet extractor, the $CHCl_3$ was removed, and the residue was dried under vacuum to yield 760 mg of 95% head-to-tail coupled poly(3-hexylthiophene) (36% yield). The most recent preparation (PHT precipitated with hexane) resulted in 98% HT-HT-coupled PHT: 1H NMR ($CDCl_3$) 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); ^{13}C NMR (1H decoupled) 140.0, 134.0, 130.5, 128.5, 31.8, 30.5, 29.5, 29.3, 22.8, 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), 137.0 (0.01); UV-vis ($CDCl_3$) λ_{max} , 442 nm; band edge 550 nm. (Film, cast from $CHCl_3$) 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 (M_w) of around 10 000, with a polydispersity of 1.6. A CS_2 -soluble fraction (insoluble in $CHCl_3$ and THF) is a HT-HT-coupled PHT with an identical 1H NMR to the $CHCl_3$ -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 18 mmol scale; however, after stirring for 15 h, 0.41 mol % of $Ni(dppp)Cl_2$ 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, H_2O , and MeOH again. The solid was dried under vacuum and Soxhlet extracted with MeOH and hexanes. The polymer was then dissolved in $CHCl_3$ using a Soxhlet extractor, the $CHCl_3$ was removed, and the residue was dried and yielded 2.28 g of 96% head-to-tail coupled poly(3-octylthiophene) (65% yield). The most recent preparation gave 97% HT-HT-coupled POT: 1H NMR ($CDCl_3$) 6.90 (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), 2.50 (m, 0.04 H); ^{13}C NMR (1H decoupled) 140.0, 133.8, 130.6, 128.5, 31.9, 30.0, 29.6, 29.3, 29.0, 23.0, 14.2; the relative intensity of the small absorptions (relative to the 128.5 absorption) are 140.3 (0.03), 134.8 (0.004), 127.2 (0.02), 126.7 (0.009); UV-vis ($CDCl_3$) λ_{max} 446 nm; band edge 575 nm. (Film, cast from $CHCl_3$) λ (relative intensity) 520 (1.6), 553 (1.6), 603 (1.0), band edge 675 nm (~1.8 eV). GPC analysis of the THF-soluble solid polymer indicates a average molecular weight (M_w) of around 24, 424 with a polydispersity of 1.98.

A Representative Quenching Reaction: Reaction of 2-Bromo-3-butylthiophene with LDA, Followed by Quenching with TMSCl. 2-Bromo-3-butyl-5-(trimethylsilyl)-thiophene. The quenching studies were performed on a 1.5 mmol scale, and the 2-bromo-3-butyl-5-lithiothiophene was generated in a procedure identical to the polymerization reactions. 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

(40) It is worth noting that in the case of excess *n*-BuLi, as expected, we have observed an increase number of nonregioispecific couplings, and in the cases of "old" and probably wet $MgBr_2 \cdot OEt_2$ and $Ni(dppp)Cl_2$, we have obtained either very low yields or no observed polymer formation.

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 *t_R* = 12.42 min) and 1% of 2-(trimethylsilyl)-3-butyl-5-bromothiophene (6.95 ppm, GC *t_R* = 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-lithio species and MgBr₂·OEt₂ 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.