Regioregular, Head-to-Tail Coupled Poly(3-alkylthiophenes) Made Easy by the GRIM Method: Investigation of the Reaction and the Origin of Regioselectivity

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ABSTRACT: An investigation of the new synthetic method to synthesize regioregular, head-to-tail coupled poly(3-alkylthiophenes) using magnesium–halogen exchange (Grignard metathesis) called the GRIM method is described. Treatment of 2,5-dibromo-3-alkylthiophenes with a variety of alkyl and vinyl Grignard reagents resulted in two metalated, regiochemical isomers, namely, 2-bromo-3-alkyl-5-bromomagnesio-thiophene and 2-bromomagnesio-3-alkyl-5-bromothiophene in an 85:15 ratio. This ratio appears to be independent of reaction time, temperature, and Grignard reagent employed. Introduction of a catalytic amount of Ni(dppp)Cl$_2$ to this isomeric mixture afforded poly(3-alkylthiophene) that contained greater than 95% HT–HT couplings (typically 98% HT couplings were seen). The high degree of regioregularity found in the polymer can be explained by a combination of kinetic and thermodynamic effects arising from steric and electronic effects found in the catalytic reaction. A series of reaction investigations led to a general explanation of the origin of regioregularity in polythiophene polymerization reactions. These reactions included kinetic studies and competition experiments.

Introduction

The ability of chemists to design and synthesize conjugated organic polymers remains the key to technological breakthroughs using polymer materials in electronic and photonic devices and the development of nanoscale devices. The synthesis of *p*-phenylenevinylene (PPV) has led to polymer LEDs.[1] The syntheses of sexithiophene, regioregular poly(3-alkylthiophene) (PAT), and *p*-thienylenevinylene (PTV) are examples of new polymers that have led to new plastic transistor applications. In all of these examples, the ease of synthesizing the material allows access of these polymers to chemists, physicists, engineers, and material scientists, which in turn leads to the development of new devices and applications of polymer-based materials.

Poly(3-alkylthiophenes) represent a class of polymers where regioregular synthesis of PATs has dramatically improved the properties of polythiophenes and has ushered in these polymers as materials in new devices. Since 3-alkylthiophene monomers are asymmetric, polymerization may occur in a nonregiospecific fashion forming three types of dyad structures (head-to-head (HH), head-to-tail (HT), and tail-to-tail (TT)) and four types of spectroscopically distinct triad structures (Figure 1). It has been shown that head-to-head couplings are unfavorable because of the steric repulsion between both alkyl chains with the lone pairs of adjacent sulfur atoms.[2] Polythiophenes that contain significant amounts of head-to-head couplings (which implies significant amounts of tail-to-tail couplings must also be present) are referred to as regioirregular, while polymers that contain only head-to-tail couplings are referred to as regioregular. Regioirregular polymers cannot readily adopt planar conformations, and irregular placement of the solubilizing alkyl substituents prevents efficient solid-state packing and limits the materials physical properties.[3] Conversely, regioregular, head-to-tail coupled poly(3-alkylthiophenes) (HT-PATs) can undergo self-

assembly, both in solution and in the solid state, resulting in highly ordered two- and three-dimensional polymer architectures. These materials have superior electronic and photonic properties when compared to regioirregular analogues.

A few years ago, our laboratory developed the first synthetic procedure to produce poly(3-substituted)-thiophenes with almost exclusive head-to-tail couplings (>98%).[3] Lithiation of 2-bromo-3-alkylthiophenes, using LDA at cryogenic temperatures followed by transmetalation with MgBr$_2$·Et$_2$O affords only one metalated regioisomer. Cryogenic temperatures are used because of the known tendency for substituted, lithiated aryl and heteroaryl halides to scramble by metal–halogen exchange at elevated temperatures, resulting in mixtures of isomeric products.[4] Polymerization in a head-to-tail fashion is achieved by Kumada coupling using catalytic amounts of Ni(dppp)Cl$_2$ (dppp = diphenylphosphino-propane) (Figure 2, method 1).[5] This method has been employed by us and other research groups to prepare other regioregular poly(3-substituted)thiophenes, random copolymers of PATs, and amphiphilic alternating copolymers of thiophene that form nanoscale electronic polymer devices by self-assembly.[6–9]

Another synthetic approach to synthesize HT-PATs was introduced by Chen and Rieke.[10] In this method, Rieke zinc, noted as Zn*, undergoes selective oxidative addition to 2,5-dibromo-3-alkylthiophenes at cryogenic temperatures to afford one regiochemical intermediate (Figure 2, method 2). This metalated intermediate undergoes regioselective polymerization in a Negishi cross-coupling reaction[11] to yield the desired HT-PAT (Figure 2, method 2). Interestingly, the percentage of head-to-tail couplings is altered dramatically by the use of other nickel and palladium catalysts.[10a,d] The regioselective control (or lack of) was rationalized on the basis of the steric congestion at the reductive elimination step in the catalytic cycle. Other monomers have also been successfully polymerized.[12,13]
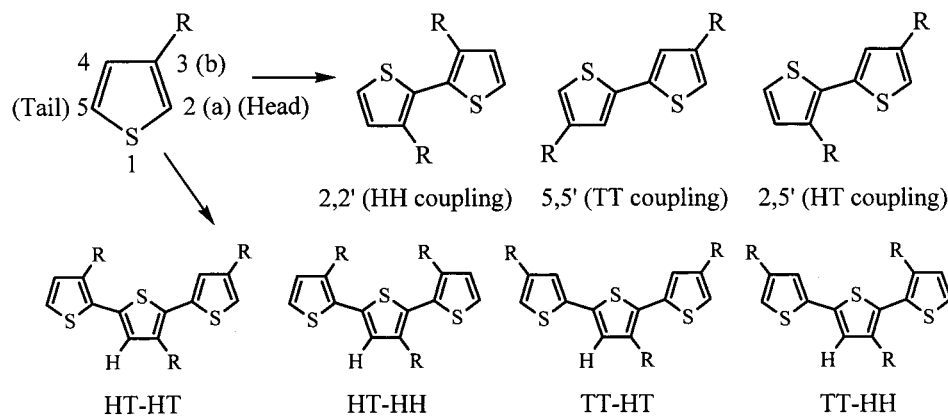
Figure 1. A 3-substituted thiophene can couple to generate three structural diads and four spectroscopically distinct triads.


[a] yields 60-75%, Mw=20K-40K, PDI=1.12-1.4.   [b] yields 67-82%, Mw=37K-49K, PDI=1.13-1.48.   [c] dppe = diphenylphosphinoethane.

Figure 2. Synthetic methods that yield HT-PATs.

More recently, Stille[14,15] and Suzuki[16,17] cross-couplings methods have been applied to the synthesis of HT-PATs (Figure 2, methods 3 and 4). Cryogenic lithiation of 2-halo-3-alkylthiophenes and subsequent treatment by organotin or organoboron electrophiles generates suitable monomers for regiospecific polymerization. These monomers undergo polymerization upon treatment with suitable palladium catalysts. One of the most powerful new synthetic methods to make regioregular polythiophenes has been developed by Iraqi and coworkers based on Stille chemistry. The Iraqi synthesis leads to a regioregular polythiophene bearing long alkyl chains terminated by a bromine. This polymer can be easily transformed into a large number of regioregular polythiophenes by simple nucleophilic displacement of the bromine atom.[18]

We have recently developed a new method to synthesize HT-PATs (Scheme 1).[19] Treatment of a 2,5-dibromo-3-alkylthiophene monomer **1** with 1 equiv of an alkyl or vinyl Grignard reagent results in a magnesium–bromine exchange reaction, also referred to as Grignard metathesis. This reaction proceeds with a moderate degree of regioselectivity leading to an 85:15 distribution of regiochemical isomers **2:3** regardless of Grignard or temperature employed. As seen in Scheme 1, the active monomer to be polymerized is trivially prepared by

Scheme 1. Synthesis of HT-PATs by the Grignard Metathesis (GRIM) Method

1a R = Butyl
1b R = Hexyl
1c Octyl
1d Dodecyl
R' = alkyl, vinyl
X = chlorine, bromine
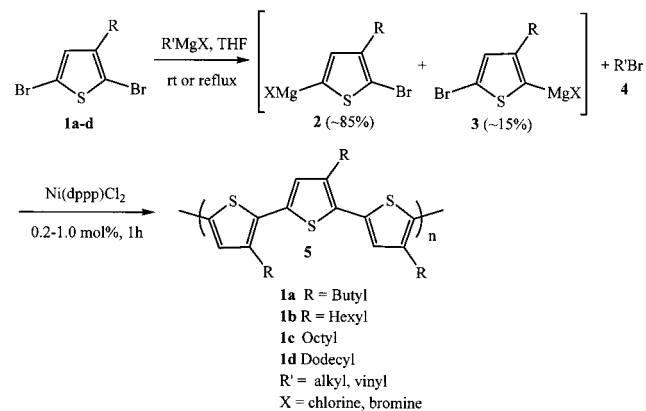
treatment of 2,5-dibromo-3-alkylthiophene with any cheap and readily available Grignard reagent solution. Treatment of this **2:3** mixture with a catalytic amount of Ni(dppp)Cl₂ affords analytically pure, highly regioregular PATs, **5**. This method can be done at room temperature or in refluxing THF and does not require cryogenic temperatures like the other methods described above. Second, reaction setup and polymerization are

quick, easy, and cost-effective. This paper presents an investigation of various reaction parameters, quenching experiments to monitor regioselectivity during the metathesis step and competition experiments, and kinetic studies used to understand regioselective polymerization from a distribution of isomers. The procedure we call the GRIM (Grignard metathesis) method is a important new synthetic method that can easily provide regioregular, head-to-tail (HT) PATs and will promote the use of this material in the development of new technologies.

Results and Discussion

Regioselectivity in the Magnesium−Halogen Exchange Reaction. 2,5-Dibromothiophene as the Monomer. The preparation of organomagnesium compounds by metal−halogen exchange (eq 1)

$$RX + R'MgX' \rightarrow RMgX' + R'X \qquad (1)$$

(aka Grignard metathesis) between Grignard reagents and organic halides has seen limited use when compared to the corresponding reaction of organolithium compounds. Nevertheless, it does work well for certain classes of compounds, notably aryl and heteroaryl bromides and iodides.[20−24] Gronowitz and co-workers did some early work on thiophene by observing metathesis in 2,5-dibromo-3-methyl and 2,5-dibromo-3-ethyl-thiophene with ethylmagnesuim bromide.[25] More recently, Cáhiez and Knochel exploited this reaction on substituted aryl iodides and bromides with isopropyl-magnesium bromide or diisopropylmagnesium to afford aryl Grignard reagents, which in the presence of electrophiles react to give excellent yields of coupled products.[26] Significantly, this exchange reaction is tolerant to a variety of functional groups (amides, esters, nitriles, alkyl halides, to name a few) at low temperatures (−25 °C and below).

When applied to 2,5-dibromo-3-alkylthiophenes **1**, Grignard metathesis is facile. The compounds 2,5-dibromo-3-alkylthiophenes are extremely convenient to prepare since simple dibromination of 3-alkylthiophenes results in the formation of 2,5-dibromo-3-alkyl-thiophenes in good yields after a very simple distillation. In THF, reaction occurs between temperatures from as low as −40 °C to reflux. Slow exchange is seen at −78 °C, and fastest exchange occurs at reflux (67 °C for THF). Generally, the reaction is run at room temperature or reflux. Treatment of **1** with 1 equiv of RMgX (R may be alkyl or vinyl group; X may be Cl or Br) results in magnesium bromine exchange. Significantly, no bis-Grignard formation is detected, even when an excess (1.2 equiv) of Grignard reagent is employed. Alkynyl and phenyl Grignard reagents were also examined, but no magnesium−halogen exchange could be observed when employing these reagents.

Table 1 shows the quenching results of some bromine−magnesium exchange reactions on 2,5-dibromo-3-hexyl-thiophene (**1b**). Similar results are seen when using 2,5-dibromo-3-dodecylthiophene (**1d**) (not shown). Similar values upon treatment of 2,5-dibromo-3-methyl and 2,5-dibromo-3-ethylthiophene with ethylmagnesuim bromide have been reported.[25] Treatment of 2,5-dibromo-3-hexylthiophene with 1 equiv of a variety of Grignard reagents and quenching these intermediates with water affords products **6** and **7** (Table 1). As a check of the results, quenching with chlorotrimethylsilane was also employed in some cases with similar results. Regio-

Table 1. Quenching Results of Magnesium−Bromine Exchange Reactions

Trial	R	X	%6:%7
1	Methyl	Br	88:12
2	Ethyl	Cl	85:15
3	Propyl	Cl	85:15
4	Butyl	Br	84:16
5	Hexyl	Cl	83:17
6	Dodecyl	Cl	85:15
7	Cyclohexyl	Cl	81:19
8	i-Propyl	Cl	80:20
9	t-Butyl	Cl	85:15
10	vinyl	Br	88:12

Scheme 2. Halogen−Magnesium Exchange and Subsequent Polymerization Can Also Be Applied to 2-Bromo-3-dodecyl-5-iodothiophene, 9
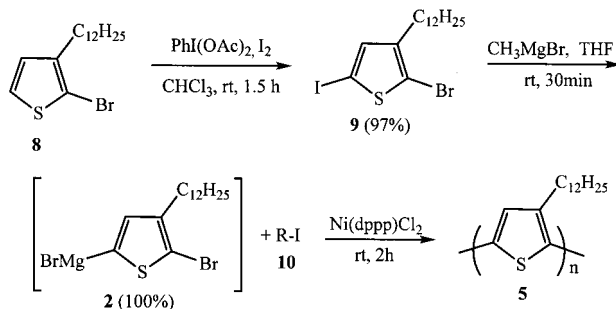

selectivity was determined by GC/MS and, in many cases, ^{1}H NMR. In all trials, the regiochemical distribution of isomers (**6:7**) was found to be approximately 85:15, regardless of the Grignard reagent used. Apparently due to sterics, there is some degree of regioselectivity displayed, with exchange favored at the 5-position of the thiophene. This ratio also appears to be independent of reaction temperature.

We have also checked for the production of the alkyl (or vinyl) bromide byproduct, **4**. Production of **4** was confirmed by GC/MS in trials 4−7. Sterically bulkier i-Pr and t-Bu Grignard reagents (trials 8 and 9) produce similar isomeric ratios; however, starting material **1** is detected for both trials, suggesting that possible side reactions may be supported by the use of these Grignard reagent. The use of vinylmagnesium bromide (trial 10) also yielded unreacted starting material. Nevertheless, for these trials (8−10), subsequent polymerization with Ni(dppp)Cl₂ also affords regioregular poly(3-alkyl-thiophenes), making these reagents suitable for this reaction.

2-Bromo-3-alkyl-5-iodothiophene as the Monomer. Halogen−magnesium exchange was also performed on 2-bromo-3-dodecyl-5-iodothiophene, **9** (Scheme 2). Monomer **9** was synthesized by regioselective iodination of 2-bromo-3-dodecylthiophene, **8**, using iodoben-zene diacetate and iodine. This method is superior to HgO/I₂[27] and HNO₃/I₂[28] reagent systems generally used on aryl species. A slight stoichiometric excess of iodine ensures complete conversion into product without iodi-nating the vacant 4-position. The byproduct, iodoben-zene, can easily be removed by distillation. Treatment of **9** with 1 equiv of methylmagnesium bromide at room temperature for 30 min resulted in the exclusive forma-

**Scheme 3. Polymerization Is Unsuccessful When Using 11 as the Monomer**
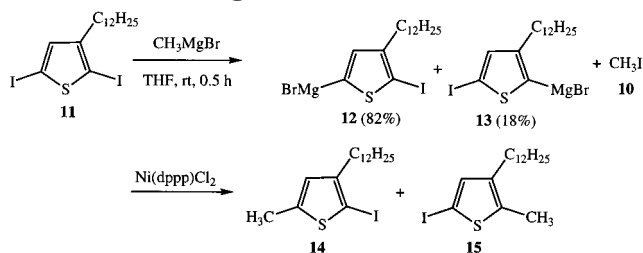
Scheme 4. No Polymerization Occurs When *tert*-Butylmagnesium Chloride Is Employed To Polymerize 11

Figure 3. Effect of metal and ligands on regioselectivity.

Figure 4. Polymerization with Ni(cod)$_2$.
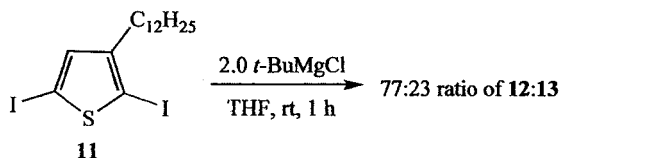
tion of **2**. Quenching of the reaction followed by GC/MS showed that no starting material or isomer **3** was present, indicating regiospecific exchange between the Grignard reagent and the thienyl iodide. This intermediate can also be polymerized with Ni(dppp)Cl$_2$ to yield HT-PDDT in 47% yield (CHCl$_3$ fraction) ($M_n = 21$K; PDI = 1.36 by GPC). However, this method shows no advantage over polymerization of the **2** and **3** which are generated from **1**, since 2,5-dibromo-3-alkylthiophene is very easy to prepare.

2,5-Diiodo-3-alkylthiophene as the Monomer. Lastly, halogen−magnesium exchange was performed on 2,5-diiodo-3-dodecylthiophene, **11** (Scheme 3). This compound was prepared by diiodination of 3-dodecyl-thiophene using iodobenzene diacetate and iodine as described above. The reaction was performed at room temperature for 30 min before an aliquot was removed and quenched with water. GC/MS found the ratio of regiochemical isomers **12**:**13**, to be about 85:15, similar to the ratios found for 2,5-dibromo-3-hexylthiophene shown in Table 1. No bis-Grignard formation or starting material was detected, suggesting a complete metathesis. However, subsequent polymerization with Ni-(dppp)Cl$_2$ afforded no polymer, and only 2-iodo-3-dodecyl-5-methylthiophene (**14**) and 2-methyl-3-dodecyl-5-iodo-thiophene (**15**) were recovered in a 79:21 ratio as determined by GC/MS. The methyl iodide byproduct from exchange, **10**, is very active for cross-coupling and presumably couples with the thienyl Grignard reagent, preventing polymerization (eq 2).

$$RMgBr + CH_3I + Ni \rightarrow R-CH_3 + MgBrI \quad (2)$$
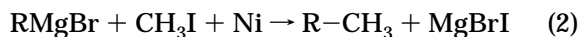
Because of this "capping" reaction between methyl iodide and the thienyl Grignard reagents, the use of *tert*-butylmagnesium chloride was explored (Scheme 4). The byproduct of this metathesis, *tert*-butyl iodide, is too sterically hindered to cross-couple with the thiophene Grignard reagent,[26] and successful polymerization should occur. However, addition of Ni(dppp)Cl$_2$ failed to yield appreciable quantities of polymer. The recovered products indicated that no reaction took place. Currently it is unclear why no cross-coupling occurred. At this point, it appears that successful polymerizations occur with monomers **1** and **9**, but not with monomer **11**.
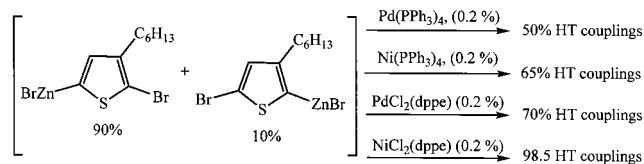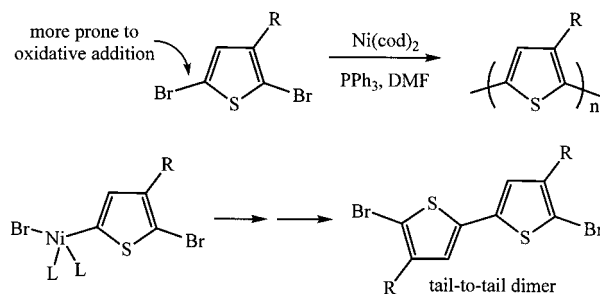
Reaction Parameters. We have observed a few problems side reactions in the GRIM method. The use of more than 1 equiv of methyl Grignard can lead to methyl end group capping as determined by MALDI-MS.[47] In addition, we have observed that polymerization temperature is perhaps the most critical parameter in controlling end group composition. Specifically, poly-merizations which are carried out in refluxing THF are often found to contain several types of end group types, some which have not yet been accounted for. We have observed phenyl group transfer from the catalyst to the polymer (H/Ph. Ph/Br) as well as desulfurization by the catalyst on the terminal thiophene ring (H/3-alkyl-1,3-butadiene). Polymerizations carried out at room temperature afford much cleaner MALDI spectra and simpler end group structural types.

Catalyst Selectivity. Although there is a moderate degree of selectivity for bromine−magnesium exchange (85:15 ratio of **2**:**3**) displayed by 2,5-dibromo-3-alkyl-thiophenes, all of the resultant poly(3-alkylthiophenes) synthesized have around 95−98% head-to-tail couplings. How can a mixture of two regiochemical isomers yield PATs with near 100% head-to-tail couplings?

While it has been shown in the synthesis of HT-poly-(3-alkylthiophenes) that catalyst choice is critical in determining the % HT couplings in the resultant polymer in a method developed by Rieke, where a ratio of **2**:**3** is 90:10.[10a,d] It was shown that catalysts with sterically demanding ligands (like dppe and dppp) and small metal centers like Ni afford poly(3-alkyl-thiophenes) with a high degree of regioselectivity (>98.5% HT couplings). Less bulky, labile ligands like PPh$_3$ combined with larger metal centers like Pd lead to a regiorandom sample of poly(3-alkylthiophenes) (Figure 3). However, these results do not fully explain the regioselectivity of the polymerization.

Other reports have found that the oxidative addition of Ni(cod)$_2$ (cod = 1,5-cyclooctadiene) to 2,5-dibromo-3-alkylthiophenes[29] occurs preferentially at the 5-position of the thiophene ring due to the limited degree of steric hindrance (as compared to the 2-position) (Figure 4). Again, these results do not explain the regioselectivity of the polymerization.

In the GRIM method, the same chemistry as described above plays some role in the resultant production of regioregular HT-PATs. Figure 5 suggests that the steric congestion on the catalyst may prevent the
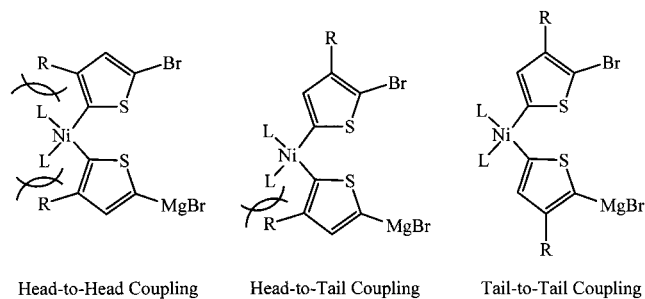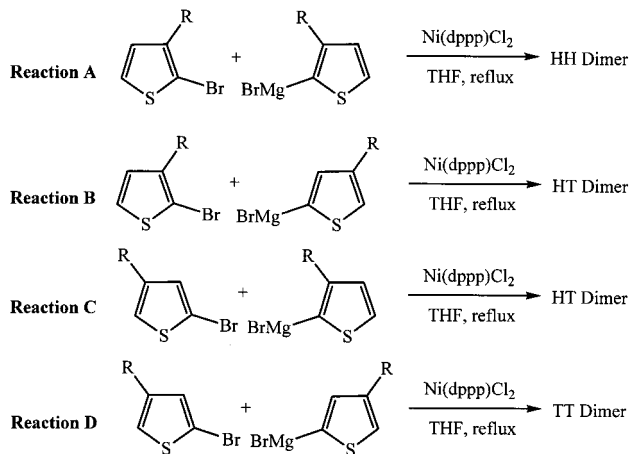
Figure 5. There is a varying degree of steric congestion after formation of catalyst intermediate.

Scheme 5. There Are Four Ways That 3-Substituted Thiophene Monomers May Couple

Figure 6. Plot of percent dimer formation as a function of time for each possible dimerization reaction.

formation of catalyst intermediate leading to HH coupling, while the lack of steric interactions upon forming the catalyst intermediate leading to TT and HT couplings is favorable (Figure 5). Reasoning by analogy GRIM should have similar chemistry for the oxidative addition step as the reaction in Figure 3. The Ni(cod)$_2$ reaction suggests that a 5-metalated isomer should have a faster rate of oxidative addition than the 2-metalated isomer due to the limited amount of steric strain associated with the 5-position.

Kinetics of Thiophene Dimerization Reactions. We ran a series of dimerization reactions between all possible thiophene-coupling partners that mimic the first step in the polymerization and subsequently examined the relative rates of dimer formation (Scheme 5). There are four different ways in which 3-substituted thiophenes can couple to form dimers. A 2-bromo-3-alkylthiophene can cross-couple with a 2-bromomagnesio-3-alkylthiophene (reaction A) to give a head-to-head coupling or 2-bromo-3-alkylthiophene can couple with a 5-bromomagnesio-3-alkylthiophene (reaction B) reagent to yield a head-to-tail dimer. Conversely, a 5-bromo-3-alkylthiophene isomer can couple with a 2-bromomagnesio-3-alkylthiophene (reaction C) to give a head-to-tail coupling or a 5-bromo-3-alkylthiophene can couple with a 5-bromomagnesio-3-alkylthiophene (reaction D) reagent to yield a tail-to-tail dimer. Prior to these studies, it was expected that reactions C and D should have relatively fast cross-coupling rates since oxidative addition occurs at the less hindered 5-position for these dimerizations. Moreover, reaction D should have the fastest relative rate of dimerization due to the limited amount of steric demand required at the reductive elimination step. Reactions A and B, on the other hand, were expected to have slower relative rates of
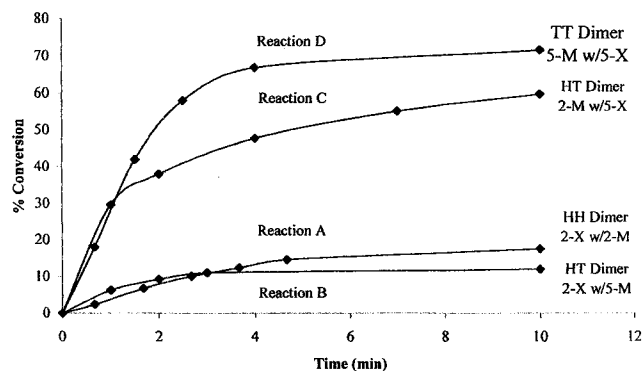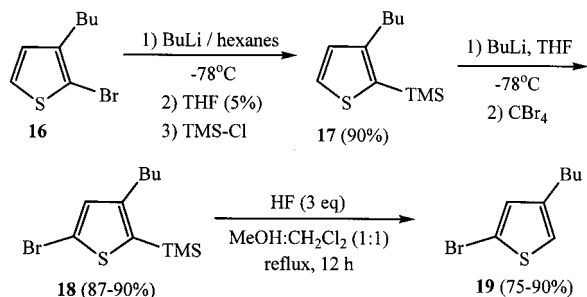
dimerization because oxidative addition for these reactions occurs at the more sterically hindered 2-position of the thiophene ring. Reaction A was expected to have the slowest relative rate of dimerization because of steric strain in the transition stat of the reductive elimination step (Figure 5).
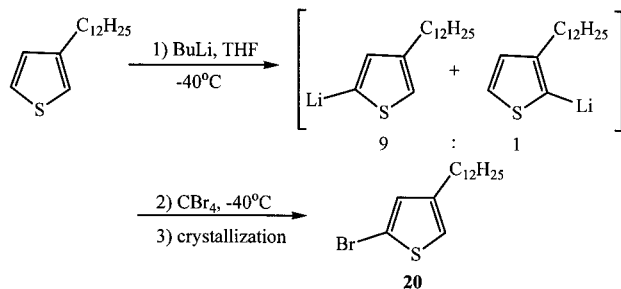
Synthesis of 2-Bromo-4-alkylthiophene. Before these dimerization reactions could be carried out, a synthesis for 2-bromo-4-alkylthiophenes had to be realized. Compound 2-bromo-3-butylthiophene (**16**) was treated with butyllithium in hexanes at −78 °C followed by addition of a small quantity of THF (∼5% vol based on hexanes) which results in precipitation of 2-lithio-3-butylthiophene. Quenching with chlorotrimethylsilane[30] afforded **17** in 90% yield. Product **17** was then treated with butyllithium in THF at −78 °C, followed by quenching with carbon tetrabromide. After several attempts with low to moderate yields (30−50%), it was realized that slow addition of CBr$_4$ (as a solution in THF) to the reaction solution was necessary; otherwise, side reactions became apparent. The use of 0.67 equiv of CBr$_4$ was found to work best.[31] These modifications allowed for preparation of **18** in 87−90% yields. Removal of the TMS blocking group was needed to generate the isomer, **19**. This turned out to be more tedious than expected. Treatment of **18** with tetrabutylammonium fluoride on silica (TBAF) was efficient at cleaving the TMS group but completely scrambled the thiophene species, resulting in a 1:1 mixture of 2-bromo-3-butyl- and 2-bromo-4-butylthiophene. TBAF, as a solution in THF, also afforded the same result. Even cryogenic temperatures (−78 °C) did not suppress isomer formation. It was realized that a desilylation method needed to be employed which suppresses the formation of carbanions, which have a tendency to scramble in these systems. Hydrofluoric acid was found to be a suitable choice for desilylation without scrambling. Treatment of **18** with an excess (3 equiv) of HF in methanol: methylene chloride (1:1) at reflux gave product **19** as a pure isomer in 75−90% yields.

Kinetic Studies. Scheme 5 shows the dimerization reactions that were employed in a series of kinetic studies. All of the dimerization reactions were performed in refluxing THF. The monomer concentration was 0.20 M. A catalytic amount, 0.5 mol %, of Ni catalyst was employed in all cases. Aliquots (0.5 mL) were removed at various time intervals and examined by GC/MS. Integration of the dimer product vs the halogenated starting material was used to determine the percent conversion from monomer to dimer. Figure 6 shows a plot for the percent conversion from monomer into dimer

Scheme 6. Synthesis of 2-Bromo-4-butylthiophene

Scheme 7. Direct Synthesis of 2-Bromo-4-dodecylthiophene

Scheme 8. Competition Experiments between Thiophene Isomers in Cross-Coupling

Table 2. Results from Competition Experiments

| reaction | % conv | products[a] | | |
		TT dimer	HT dimer	HH dimer
E	70	80	20	0
F	28	13[b]	80	7
G	65	53	47	0
H	21	5	90	5

[a] Based on percent conversion. [b] Due to homocoupling.

vs time for reactions A, B, C, and D (Scheme 5). Reactions C and D yielded the fastest relative rates of dimerization. Reaction D also gives good conversion as expected with 70% conversion in 10 min and 88% conversion seen in 2 h. Reaction C appears to have a similar initial reaction rate to reaction D but then slows down when compared to Reaction D. Conversely, reactions A and B were found to give slower relative rates of dimerization. Reaction A showed 18% conversion after 10 min. After 20 h at reflux, the percent conversion never exceeded 35%. It appears that reaction B also has a slow reaction rate. The results from Figure 6 are a good indication that there is some degree of catalyst selectivity during cross-coupling to make poly(3-alkyl-thiophenes).[32]

Competition Experiments. Competition experiments were also performed to determine selectivity. These experiments required the synthesis of 2-bromo-4-dodecylthiophene, **20**, which is employed in the competition experiments to be described, was possible by direct lithiation of 3-dodecylthiophene followed by reaction with CBr$_4$ (Scheme 7). The crude product consisted of 3-dodecylthiophene and both isomers in a 9:1 ratio. After removal of the starting material, recovery of pure 2-bromo-4-dodecylthiophene was possible by low-temperature crystallization from acetone. However, the overall reaction yields from direct preparation of the isomer were always low (20-30%) (due to side reactions and poor recovery from the crystallization procedure).

Scheme 8 shows the four reactions performed (reactions E, F, G, and H). For these reactions, an organozinc species was employed to serve as the organometallic cross-coupling partner. We chose to employ an organozinc species because of its lesser tendency to homocouple—which greatly complicated early experiments. All reactions were performed at room temperature and were allowed to react for 24 h. All products were analyzed by ^{1}H NMR. Reactions E and F utilize a 1:1 mixture of both organozinc isomer intermediates (**21** and **22**). To these mixtures is added 1 equiv of a brominated thiophene monomer (**8** or **20**). Reactions G and H utilize a 1:1 mixture of brominated thiophene

monomers (**8** and **20**). To these mixtures is added 1 equiv of a monometalated organozinc thiophene isomer (**21** or **22**).

Table 2 displays the results from reactions E–H. Reaction E, which is expected to generate a mixture of tail-to-tail and head-to-tail coupled dimers, has the highest percent conversion after 24 h. The results show that 4 times as much TT dimer is produced as compared to the HT dimer, and this result is most likely due to the sterics of the catalyst formation in the reductive elimination step. Reaction F, which is expected to generate a mixture of head-to-tail and head-to-head coupled dimers, has moderate percent conversion after 24 h and is likely due to the slowed oxidative addition step at the 5-position. Recovery of the dimeric products shows that all three dimers are present. There is nearly 10 times more HT dimer than HH dimer. Despite the homocoupling reaction being poor for organozincs, we also see some TT coupled dimer that is a product of homocoupling.

Reaction G, like reaction E, has moderate percent conversion into dimeric products and is likely due to the fact that tail-to-tail couplings may be formed in this reaction. Reaction H, like reaction F, has a low percent conversion into dimeric species and a high selectivity for formation of head-to-tail coupled dimers. Like reaction F, we also observe some TT dimer. The competition reaction results and the kinetic data presented strongly suggest that the catalyst is biased in which coupling partner (i.e., which isomer) it will react with and that the thermodynamics of the product formation plays a role in determining product formation in the coupling reactions.[32]

A Model To Explain Regioselectivity in the GRIM Polymerization Method. From the above

Polymerization Pathways That Give Only Polythiophenes With 100% Head-to-Tail Couplings

"Good" isomer reacting with "Good" isomer polymerization pathways
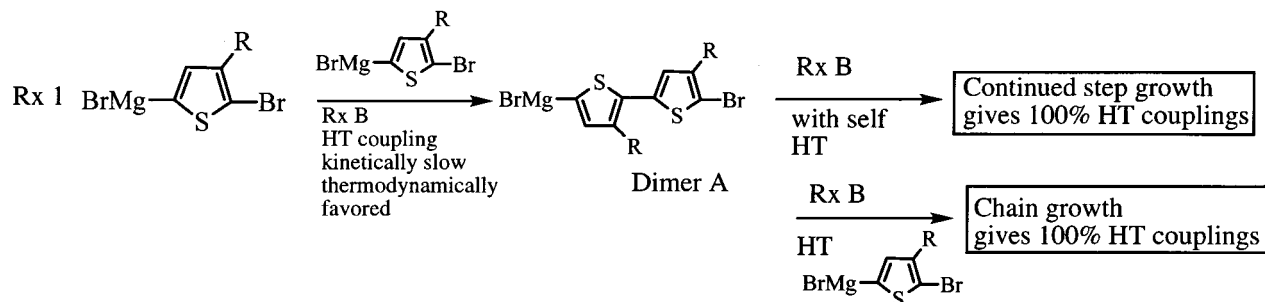
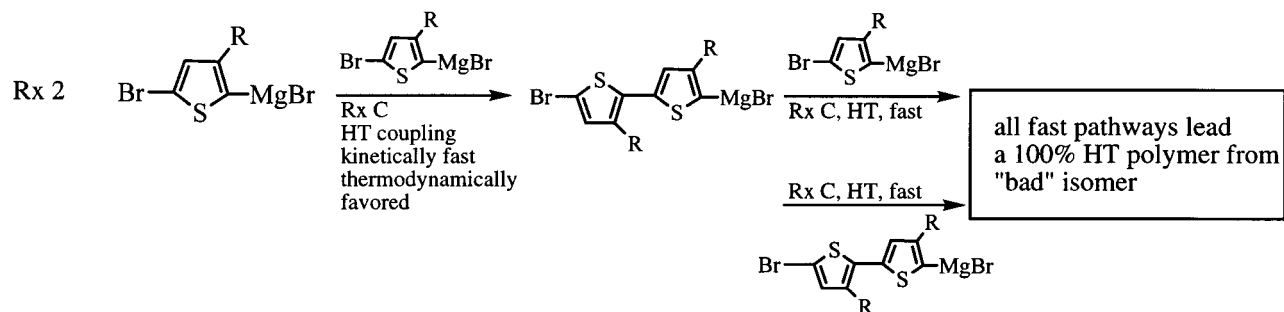"Bad" isomer reacting with a "Bad" isomer polymerization pathways

Figure 7. Polymerization pathways for the GRIM method.

kinetic studies and competition reaction studies emerges a picture that can be used to explain regioselectivity in the GRIM polymerization method. Basically, there are two major reaction pathways that lead to a fully regioregular head-to-tail (HT) coupled poly(3-alkyl-thiophene) (PAT) structure as shown in Figure 7. Examining the polymerization pathway for reaction 1 (Figure 7), we can find that a self-reaction (and self-polymerization) of the "good" isomer, compound **2**, can lead to a fully HT-coupled PAT by either a step growth or a chain growth polymerization mechanism. As shown in the kinetic studies (Figure 6), while reaction B is kinetically slow under the conditions of the reaction, the reaction is favorable thermodynamically by forming a conjugative dimer (and polymer in the polymerization). Competition reaction G also shows that reaction B competed with kinetically fast reaction D by forming almost equivalent amounts of HT dimer as TT dimer as indicated byproduct ratios in Table 2. In addition, we have observed that more highly conjugated intermediates react faster with the catalyst than the monomer.

In reaction 2 (Figure 6), a very interesting reaction is considered. It appears that that a self-reaction of the "bad" isomer, compound **3**, can lead to a fully HT-coupled PAT by either step growth or chain growth polymerization mechanism. All the polymerization steps would occur by the kinetically fast reaction C and would be thermodynamically favored by the formation of a growing conjugated chain. Competition reactions E and H also show this process occurs. This appears to be the dominant reason that, despite having 15% of the "bad" isomer, compound **3**, the PATs produced from the GRIM method have around 95–98% head-to-tail couplings.

In reaction 3 (Figure 8) is shown a polymerization pathway where a "bad" isomer compound **3** can react with a "good" isomer, compound **2**, to form one TT coupling. In this pathway, kinetically favorable reaction

D and reaction C can give polymer. However, assuming that HH couplings are not competitive for kinetic and thermodynamic reasons (reaction 4), then once a TT coupling forms, the polymer can only grow in an HT fashion. This leads to a polymer with only one TT defect. This type of TT defect reaction can also occur in reactions 1 and 2; however, the worst possible case is 15% defect couplings in the resultant polymer structure. It appears, however, that reactions 1 and 2 are operative and lead to an HT-PAT with 95–98% HT couplings. This explanation does not take into account the fact that HT-PAT is more crystalline than PAT with a number of defects, and the polymers with less than 95% HT couplings could possibly be washed out in the Soxhlet extraction isolation of 95% HT-PAT from the GRIM method.

Nevertheless, this series of reaction and kinetic studies shed some light on the origin of regioselectivity in the GRIM polymerization of 3-alkylthiophenes.

Conclusions

Grignard metathesis has been found to be a very quick and easy method for the synthesis of regioregular, head-to-tail coupled poly(3-alkylthiophenes). Despite the fact that Grignard metathesis gives an 85:15 ratio of **2**:**3**, polymerization using Ni(dppp)Cl$_2$ affords fully regioregular HT-PATs in good yields. Kinetic data and competition experiments strongly suggest that kinetic and thermodynamic arguments based on catalyst selectivity can support the origin of regioselectivity. This reaction is an improvement over previous methods due to its simplicity and cost-effectiveness. There is no need for expensive anhydrous zinc chloride or magnesium bromide reagents or cryogenic temperatures. This reaction has been currently being extended to include other thiophene monomers bearing esters, ethers, alkyl bromides, and alkoxy groups. This reaction can also be

Polymerization pathways where "Bad" isomer and "Good" isomer react to form 1 bad TT coupling followed by all HT coupling leading to a polymer with all HT couplings and 1 TT coupling
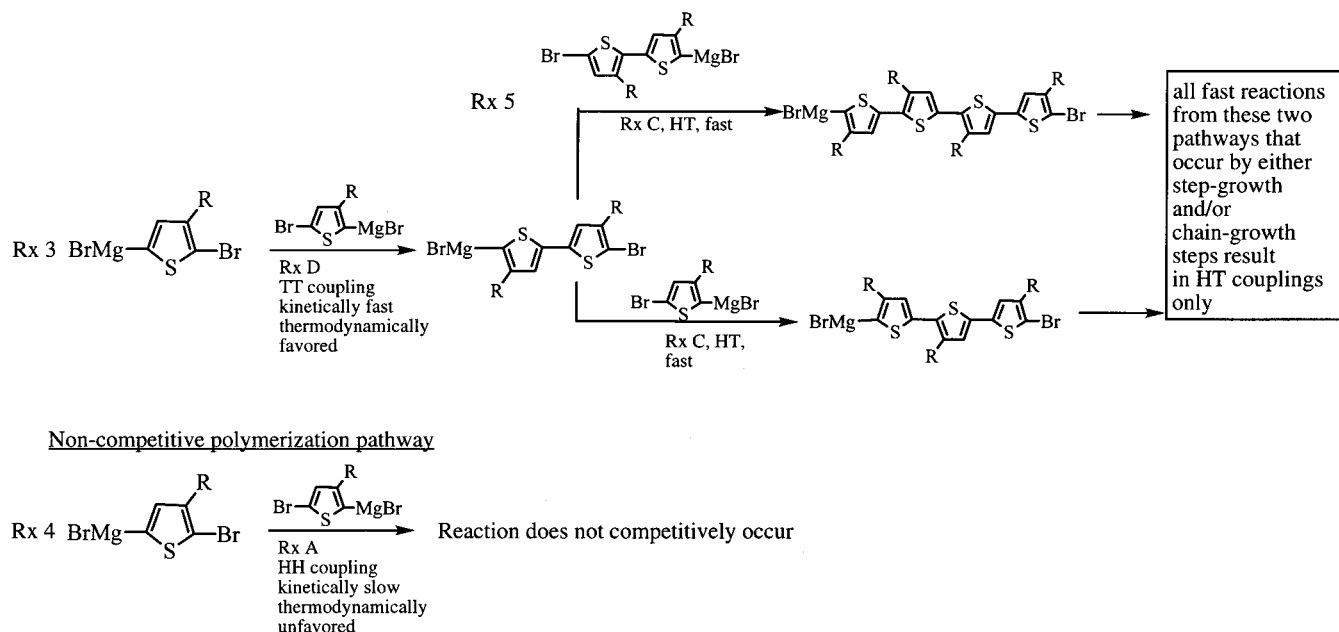

Non-competitive polymerization pathway

Figure 8. Additional polymerization pathways for the GRIM method.

applied in the synthesis of alternating copolymers as been shown by Collard[33] and Wang.[34]

Experimental Section

General. All reactions were performed under prepurified nitrogen or argon, using either flame-dried or oven-dried glassware. All glassware was assembled while hot and cooled under nitrogen or argon. THF was dried over Na/benzophenone and freshly distilled prior to use. Chloroform was stored over molecular sieves and distilled from P_2O_5. Hexane was distilled from CaH_2 prior to use. 1,1,1-Trichloroethane and 1,1,2,2-tetrachloroethane were stored over molecular sieves. NBS was recrystallized from acetic acid. Trimethylsilyl chloride was distilled from CaH_2 prior to use. Acetic acid, HF (49%), 3-bromothiophene, bromine, carbon tetrabromide, iodine, iodobenzene diacetate, Ni(dppp)Cl$_2$, and all Grignard reagents were used as received. In some cases, titration of the Grignard reagents was performed following the procedure described by Love.[35]

^{1}H and ^{13}C NMR spectra were recorded on an IBM Bruker FT300 MHz spectrometer. All NMR spectra were recorded in CDCl$_3$. All UV/vis spectra were taken on a Perkin-Elmer Lambda 900 UV/vis/NIR spectrometer. Solution UV/vis data were taken in chloroform. Solid-state UV/vis were taken from polymer films that were either drop cast or spin cast from chloroform, 1,1,1-trichloroethane, or 1,1,2,2-tetrachloroethane. MALDI-TOF MS was performed using a Voyager-DE STR BioSpectrometry Workstation by PerSeptive Biosystems. All spectra were recorded using linear ion mode, in which samples were irradiated under high vacuum using a nitrogen laser (wavelength 337 nm, 2 ns pulse). The accelerating voltage was 25 kV. Grid voltage and low mass gate were 85.0% and 500.0 Da, respectively. All GPC spectra were recorded using a Waters 6000A apparatus and a Waters R410 differential refractometer. The eleunt was THF, which was kept at 30 °C. Flow rate was 1.0 mL/min. The system was calibrated using polystyrene standards obtained from Polymer Standards Service. GC/MS 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% phenylmethylsilicone. Elemental analysis was performed by Midwest Microlab, Indianapolis, IN.

Preparation of 3-Alkylthiophenes. All 3-alkylthiophenes were prepared according to the procedure of Kumada[36] using the specific details outlined by Zimmer et al.[37] All compounds were purified by distillation and their purities checked by ^{1}H NMR, GC/MS, and elemental analysis. Yields ranged from 60 to 85%. Purity was >99%. All physical data for these compounds have been reported.[3b,29]

Preparation of 2-Bromo-3-alkylthiophenes. All 2-bromo-3-alkylthiophenes were prepared by bromination of 3-alkylthiophene by NBS in HOAc:CHCl$_3$ (1:1). All compounds were purified by distillation and their purities checked by ^{1}H and ^{13}C NMR, GC/MS, and elemental analysis. Yields ranged from 70 to 92%. Purity was >99%. All physical data for these compounds have been reported.[3b]

Preparation of 2,5-Dibromo-3-alkylthiophenes, 1a−d. All 2,5-dibromo-3-alkylthiophenes were prepared by bromination of 3-alkylthiophene by 2.2 equiv of NBS in HOAc:CHCl$_3$ (1:1). All compounds were purified by distillation and their purities checked by ^{1}H and ^{13}C NMR, GC/MS, and elemental analysis. Yields ranged from 80 to 95%. Purity was >99%. All physical data for these compounds have been reported.[10d]

2-Bromo-3-dodecyl-5-iodothiophene, 9. 2-Bromo-3-dodecylthiophene (31.05 g, 93.41 mmol) was dissolved in 250 mL of chloroform. Iodine (13.04 g, 51.38 mmol) was added, followed by iodobenzene diacetate (18.05 g, 56.04 mmol). The solution was stirred at room temperature for 1.5 h and then poured over aqueous sodium thiosulfate. The aqueous layer was washed twice with ether, and the organic layers were collected, dried, filtered, and rotovapped. The iodobenzene byproduct was removed via Kugelrohr distillation. The remaining oil was filtered through silica using hexanes as eleunt. After rotoevaporation and drying under vacuum, 41.25 g (97%) of product was obtained. ^{1}H NMR (CDCl$_3$): δ 6.94 (s, 1H), 2.51 (t, 2H), 1.50 (m, 2H), 1.25 (m, 17H), 0.87 (t, 3H). ^{13}C NMR (CDCl$_3$): δ 144.2, 137.9, 111.7, 71.0, 31.9, 29.6, 29.3, 29.2, 29.1, 28.7, 22.7, 14.1. Calcd for $C_{16}H_{26}SBrI$: C = 42.03, H = 5.73. Found: C = 42.33, H = 5.82.

2,5-Diiodo-3-dodecylthiophene, 11. 3-Dodecylthiophene (7.79 g, 30.90 mmol) was dissolved in CHCl$_3$ (100 mL). Iodobenzene diacetate (11.44 g, 35 mmol) and iodine (8.63 g, 32.0 mmol) were then added, and the solution was stirred at room temperature overnight. Workup is identical to the procedure to make **9**. Recovered 14.10 g, 91% yield of the title compound. ^{1}H NMR (CDCl$_3$) δ: 6.87 (s, 1H), 2.49 (t, 2H), 1.49 (m, 2H), 1.25 (m, 17H), 0.87 (t, 3H). Calcd for $C_{16}H_{26}SI_2$: C =

38.11, H = 5.20, I = 50.33. Found: C = 37.91, H = 4.97, I = 50.29.

2-Trimethylsilyl-3-butylthiophene, 17. 2-Bromo-3-butylthiophene (28.27 g, 129 mmol) was dissolved in 250 mL of hexane. The solution was placed in a dry ice/acetone cooling bath, and butyllithium (50 mL, 2.58 M in hexanes) was added followed by THF (20 mL). Chlorotrimethylsilane (16.38 mL, 129 mmol) was then added dropwise. The cooling bath was removed, and the solution is warmed to room temperature. The reaction was terminated by pouring over water. Ether was then added, and the aqueous phase was washed twice with ether. The organic layers were collected, dried, filtered, and rotovapped. Distillation (53 °C, 0.02 Torr) afforded the title compound (23.318 g, 85.1% yield) as a colorless oil. ^{1}H NMR (CDCl$_3$): δ 7.43 (d, 1H), 7.03 (d, 1H), 2.67 (t, 2H), 1.58 (m, 2H), 1.39 (m, 2H), 0.93 (t, 3H), 0.33 (s, 9H).

2-Trimethylsilyl-3-butyl-5-bromothiophene, 18. 2-Trimethylsilyl-3-butylthiophene (13.74 g, 64.7 mmol) was dissolved in 100 mL of THF. The solution was placed in a dry ice/acetone cooling bath, and butyllithium (25.1 mL, 2.58 M in hexanes) was added. After 1 h, CBr$_4$ (14.37 g, 43.3 mmol) in THF (30 mL) was added dropwise by an addition funnel. After 2 h, the solution was poured over ice water. Ether was then added, and the aqueous layer was extracted twice with ether. The organic layers were collected, dried, filtered, and rotovapped. Distillation (89 °C, 0.025 Torr) afforded the title compound (17.03 g, 90.4% yield) as a colorless oil. ^{1}H NMR (CDCl$_3$): δ 6.94 (s, 1H), 2.61 (t, 2H), 1.53 (m, 2H), 1.37 (m, 2H), 0.92 (t, 3H), 0.29 (s, 9H).

2-Bromo-4-butylthiophene, 19. 2-Trimethylsilyl-3-butyl-5-bromothiophene (3.19 g, 10.9 mmol) was dissolved in 40 mL of methanol/methylene chloride (1:1). Hydrofluoric acid (0.50 mL, 49% in water) was added, and the solution was heated to reflux overnight. The reaction was terminated by pouring over water. Extraction with ether followed by rotoevaporation and distillation (55 °C, 0.025 Torr) afforded the title compound (1.76 g, 73% yield) as a colorless oil. ^{1}H NMR (CDCl$_3$) δ: 6.86 (d, 1H), 6.78 (d, 1H), 2.54 (t, 2H), 1.55 (m, 2H), 1.32 (m, 2H), 0.91 (t, 3H). Calcd for C$_8$H$_{11}$SBr: C = 43.85, H = 5.06, Br = 36.46. Found: C = 43.90, H = 5.13, Br = 36.42.

2-Bromo-4-dodecylthiophene, 20. Dodecylthiophene (16.89 g, 66.90 mmol) was dissolved in 100 mL of THF. The solution was placed in a dry ice/acetonitrile cooling bath, and butyllithium (34.5 mL, 2.5 M solution in hexanes) was added. After 1 h, CBr$_4$ (22.19 g, 66.90 mmol) in THF (20 mL) was added dropwise over a period of 30 min. The solution was stirred at −40 °C for 2 h and then poured over ice. Ether was then added, and the aqueous phase was washed twice with ether. The organic layers were collected, dried, filtered, and rotovapped down to a black oil. Removal of CBr$_4$ and starting materials was achieved by distillation. The product was crystallized from acetone (to remove 2-bromo-3-dodecylthiophene) to yield the title compound (5.2 g, 23% yield). ^{1}H NMR (CDCl$_3$): δ 6.86 (d, 1H), 6.78 (d, 1H), 2.52 (t, 2H), 1.56 (m, 2H), 1.25 (m, 17H), 0.87 (t, 3H). Calcd for C$_{16}$H$_{27}$SBr: C = 57.82, H = 8.18, Br = 24.04. Found: C = 57.21, H = 8.42, Br = 23.72.

General Aspects on the HH, HT, TH, and TT Kinetic Studies. 2-Bromo-3-butylthiophene and its isomer, 2-bromo-4-butylthiophene, were used to generate all possible dimer structures. The Grignard reagents were prepared by treatment of one of the above isomers with 1 equiv of magnesium metal. After Grignard formation was complete, addition of 1 equiv of the other isomer along with catalyst initiated the cross-coupling reaction. All reactions were done on a 0.2 M scale using 0.5 mol % of catalyst. Aliquots of 0.5 mL were removed at various time intervals, and the results were monitored by GC/MS.

General Aspects on the Synthesis of HT-PATs Using Grignard Metathesis, GRIM. All polymerizations were carried out in THF. Monomer concentrations were typically between 0.1 and 0.3 M. All polymerizations were carried out at room temperature or reflux. All Grignard reagents were purchased as a 1.0, 2.0, or 3.0 M solution in one of the following solvents: THF, diethyl ether, or dibutyl ether. The amount of Ni(dppp)Cl$_2$ catalyst added varied between 0.2 and 1.0 mol %.

All polymerizations were terminated by pouring over methanol. The resulting polymer precipitate was filtered through a Soxhlet thimble followed by Soxhlet extractions by some or all of the following solvents: methanol, acetone, hexanes, methylene chloride, THF, and chloroform.

Representative Synthesis of HT-PATs by GRIM. 2,5-Dibromo-3-hexylthiophene (1.41 g, 4.33 mmol) was dissolved in 25 mL of THF (resulting in a 0.17 M solution). To this solution was added dodecylmagnesium bromide (4.33 mL, 1.0 M solution in diethyl ether). The mixture was heated to reflux for 1 h at which time Ni(dppp)Cl$_2$ (6 mg, 0.5 mol %) was added. After 45 min at reflux, the reaction was poured over 120 mL of methanol and then filtered through a Soxhlet thimble, which was then subjected to Soxhlet extractions with methanol, hexanes, and chloroform. The polymer was recovered from the chloroform fraction by rotary evaporation. The purple solid was pumped on for 2 h to yield 478 mg (71%) of 99% HT-coupled poly-3-hexylthiophene. ^{1}H NMR (CDCl$_3$) δ: 6.96 (s, 1H), 2.79 (t, 2H), 1.70 (m, 2H), 1.35 (m, 5H), 0.90 (t, 3H). ^{13}C NMR (CDCl$_3$) δ: 139.9, 133.8, 130.5, 128.6, 31.9, 30.4, 29.5, 29.2, 22.6, 14.1. Calcd for C$_{10}$H$_{14}$S: C = 72.25, H = 8.49, S = 19.28. Found: C = 70.44, H = 8.49, S = 17.63. 1.78% of bromine was found (presumably as end group bromide).

Room Temperature Synthesis of HT-PATs by GRIM. 2,5-Dibromo-3-hexylthiphene (2.56 g, 7.86 mmol) was dissolved in 5 mL of THF. To this solution is added 4.13 mL (4.13 mmol) of cyclohexylmagnesium chloride (2.0 M in ether). After 5 min another 40 mL of THF was added followed by Ni(dppp)Cl$_2$ (15 mg). The solution was stirred for 15 min at which time it was poured over 150 mL of methanol. The polymer was recovered as above with 652 mg (51% yield) of polymer recovered from the chloroform fraction, with >95% HT coupling.

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