

MECHANISTIC ASPECTS OF REGIOREGULARITY IN HEAD-TO-TAIL COUPLED POLY(3-ALKYLTHIOPHES)

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Introduction

Poly(3-alkylthiophenes) represent a class of polymers where regioregular synthesis of PATs has dramatically improved 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 non-regiospecific 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.¹ Polythiophenes which contain significant amounts of head-to-head or tail-to-tail couplings are referred to as regiorregular, while polymers which contain only head-to-tail couplings are referred to as regioregular. Regiorregular 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. 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 regiorregular analogues.

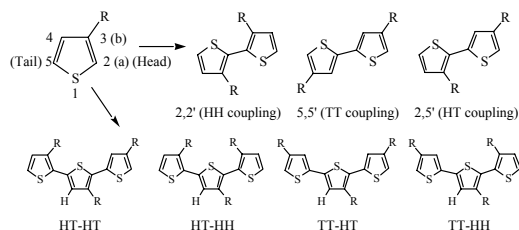


Figure 1. Combinations of coupling for poly(3-alkylthiophenes)

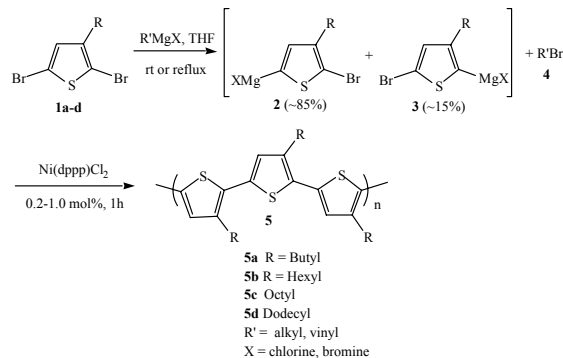
A few years ago, our laboratory developed the first synthetic procedure to produce poly(3-substituted)thiophenes with almost exclusive head-to-tail couplings (>98%).² This method has been employed by us and other research groups to prepare other regioregular poly(3-substituted)thiophenes, random copolymers of PATs, and amphiphilic alternating copolymers of thiophene that form nanoscale electronic polymer devices by self-assembly.³⁻⁶

In 1992, a method to synthesize HT-PATs have been introduced by Chen and Rieke.⁷ Rieke zinc was shown to undergo selective oxidative addition to 2,5-dibromo-3-alkylthiophenes at cryogenic temperatures to afford the desired HT-PAT through a Negishi cross-coupling reaction.⁸ 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.^{9,10}

More recently, Stille^{11,12} and Suzuki^{13,14} cross-couplings methods have been applied to the synthesis of HT-PATs. One of the most powerful new synthetic methods to make regioregular polythiophenes has been developed by Iraqi and co-workers 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.¹⁵

We have recently developed a new method to synthesize HT-PATs (Scheme 1).¹⁶ Treatment of a 2,5-dibromo-3-alkylthiophene monomer, **1**, with one equivalent 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 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 analytical 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. Secondly, reaction setup and polymerization is quick, easy, and cost effective. This paper presents an investigation of this reaction and the effect of the outcome on various parameters, including quenching experiments to monitor regioselectivity during the metathesis step, and competition and kinetic studies used to understand regioselective polymerization from a distribution of isomers. The procedure we call the GRIM (Grignard Metathesis) method is an 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.



Scheme 1

Experimental

General. All reactions were performed under prepurified nitrogen or argon, using either flame-dried or oven-dried glassware. All solvents were distilled prior to use and all reagents were used as received. In some cases, titration of the Grignard reagents was performed following the procedure described by Love.¹⁷

¹H and ¹³C NMR spectra were recorded on an IBM Bruker FT300 MHz spectrometer. All NMR spectra were recorded in CDCl₃. All UV/Vis spectra were taken on a Perkin Elmer Lambda 900 UV/Vis/NIR Spectrometer. MALDI-TOF MS was performed using a Voyager-DE STR BioSpectrometry Workstation by PerSeptive Biosystems. All GPC spectra were recorded using a Waters 6000A apparatus and a Waters R410 differential refractometer. The eluent 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% phenylmethyl silicone. Elemental analysis was performed by Midwest Microlab, Indianapolis, IN.

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 one equivalent of magnesium metal. After Grignard formation was complete, addition of one equivalent 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.

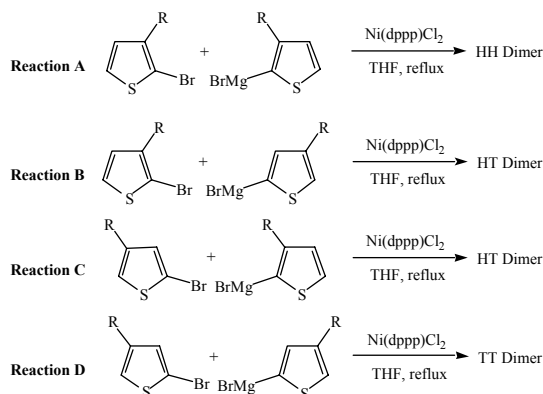
Representative synthesis of HT-PATs by GRIM. 2,5-dibromo-3-hexylthiophene (1.41 g, 4.33 mmol) was dissolved in 25 mL of THF (resulting in a 0.17 M solution). To this solution was added dodecylmagnesium bromide (4.33 mL, 1.0 M solution in diethylether). The mixture was heated to reflux for one hour at which time Ni(dppp)Cl₂ (6 mg, 0.5 mol%) was added. After 45 minutes 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 hours to yield 478 mg (71%) of 99% HT-coupled

poly-3-hexylthiophene. ^1H 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. (Calculated for $\text{C}_{10}\text{H}_{14}\text{S}$: 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).

Results and Discussion

The following discussion is a portion of the material to be presented in poster form, and discusses a kinetic study performed to determine the rates of various head-to-head, tail-to-tail, and head-to-tail couplings to form 3-alkylthiophene dimers. These reactions are envisioned to provide the basis for a model to explain regioselectivity in the GRIM polymerization method.

The kinetic and competition reaction studies illustrates in **Scheme 2** and Figure 2 emerges of the GRIM polymerization method. Basically,



Scheme 2

there are two major reaction pathways that lead to a fully regioregular head-to-tail (HT) coupled poly(3-alkylthiophene) (PAT) structure. As shown in the kinetic studies of reactions A–D, 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 is competitive with kinetically fast reaction D by forming almost equivalent amounts of HT dimer as TT dimer. In addition, we have observed that more highly conjugated intermediates react faster with the catalyst than the monomer.

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. Other competition reactions (not shown) 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.

“Bad” isomer compound **3** can react with a “good” isomer, compound **2**, to form 1 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, then once a TT coupling forms then the polymer can only grow in an HT fashion. This leads to a polymer with only 1 TT defect. This type of TT defect reaction can also occur in reactions 1 and 2, however the worse 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 applied in the synthesis of alternating copolymers as been shown by Collard¹⁸ and Wang.¹⁹

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