INTERFACIAL CROSS-COUPLING REACTIONS: THE DEVELOPMENT OF SURFACE-INITIATED KUMADA CATALYST-TRANSFER POLYCONDENSATION

by

STEPHEN KYLE SONTAG

(Under the Direction of Jason Locklin)

ABSTRACT

In this thesis, the surface-initiated polymerization of conjugated polymers using Kumada Catalyst-transfer Polycondensation (KCTP) is presented. Covalently immobilized films of conjugated polymers are fabricated on a variety of substrates and extensively characterized using spectroscopic and electrochemical techniques. This “grafting from” technique has allowed for the formation of smooth, covalently immobilized, and mechanically robust conjugated polymer films, which is not possible to obtain using grafting to and grafting through methodologies.

The grafting of conjugated polymers requires the immobilization of phosphine ligated nickel catalysts to form the polymerization initiator, which is a difficult task due to the two-dimensional nature of the interface and the close proximity of neighboring reactive sites. A technique of characterizing the grafting density using indirect electrochemical methods is presented, which has allowed for the first time to probe the behavior of surface-bound nickel species. It was found that the grafting density changes based on the ligand environment, and side reactions between neighboring initiating sites is the primary cause of the observed
low grafting density upon exchange to the necessary bidentate phosphine ligands for polymerization. Furthermore, kinetic information is also obtained from the technique and it was found that the rate of cross coupling with the immobilized initiators is dependent on the ligand environment.

To further understand the oxidative addition of Ni(0) to haloarenes, a series of kinetic isotope effect (KIE) experiments were carried out. Simple haloarenes were coupled to alkyl or aryl Grignard reagents via nickel catalysts, and analyzed for $^{13}$C enrichment using inverse gated decoupling NMR. It was found that the first irreversible step of the coupling reaction is dependent on the type of halide and position of the methyl substituent on the arene. The results presented here rationalize observations at surfaces, and also provide additional insight into the highly debated mechanism of organometallic oxidative addition reactions.

INDEX WORDS: kumada coupling, surface-initiated polymerization, conjugated polymers, interfacial reactions
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DEDICATION

To my Mom and Dad: Thank you for your unconditional support throughout my graduate studies that have propelled me to cross the finish line. I cannot thank you both enough for all your positive words of encouragement.
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CHAPTER 1

INTRODUCTION AND LITERATURE REVIEW

Introduction to Conjugated Polymers

The 2000 Nobel Prize in Chemistry was awarded to Alan Heeger, Alan MacDiarmid, and Hideki Shirakawa for the discovery of conjugated polymers (CPs).\(^1\) \(^2\) The discovery began with the observed million-fold increase in conductivity of poly(acetylene) after the addition of iodine, giving a polymer with similar characteristics to metals. In typical plastics, such as polyethylene, each carbon atom is sp\(^3\) hybridized. As a result, the energy difference between the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) is large. Such plastics are transparent to visible light and electronically insulating. However, upon sp\(^2\) hybridization, each carbon atom is linked to its neighbors by three σ bonds and one π bond. Multiple π bonds in close proximity to one another overlap, forming extended molecular orbitals with a reduced HOMO energy. Conjugated polymers have an electronic structure similar to that in inorganic semiconductors, with closely occupied levels that resemble bands. After the discovery of conductive polyacetylene in 1977, a number of CPs were reported in the literature. Some of the most common include poly(thiophene) (PT), poly(p-phenylene) (PPP), poly(phenylenevinylene) (PPV), poly(fluorene) (PF), poly(carbazole) (PCbz), and poly(pyrole) (PPy) as shown in Figure 1.1.
In the dedoped or pristine state, the bandgap of CPs falls in the semiconductor regime. Conjugated polymers can be made conductive through doping, which generates charge carriers along the polymer backbone. In general, exposing the polymer chain to an oxidizing or reducing agent can create these charge carriers. This redox reaction is often referred to as “doping”, where the use of an oxidizing agent is p-doping and the use of a reducing agent is n-doping. Conjugated polymers can also be doped electrochemically. The charge carriers generated are localized charge carriers, which is in contrast to inorganic semiconductors. Such localized charge carriers are characterized by a lattice distortion around a charge, often termed a polaron.

Since the initial discovery, the field of CPs has accelerated toward the development of new electronic devices. First and foremost, CPs are currently being exploited in the photovoltaic arena due to their electro-optical properties. Compared to inorganic semiconductors, organic materials generally have high absorption coefficients (~1000 times higher than silicon). This feature allows very thin films of CPs to absorb a large fraction of incident sunlight. Additionally,
organic materials (~1 g/cm³) also have much lower densities than silicon (2.33 g/cm³). The combination of these two main advantages promise to yield lightweight and inexpensive photovoltaic devices. With rapidly growing efficiencies, CP thin film photovoltaics are projected to revolutionize the use of solar power around the world. Other applications of CP thin films involve employment as a colorimetric or fluorescent indicator in chemical sensing, which can be applied to the creation of devices for field testing and simple assays. Several indicator systems have been created that can be chemically functionalized to enable the sensing of a tremendous range of molecules and ions. Another sensing platform can also be used involving the modification of electrodes with thin films of functionalized CPs, which show promise in chemical sensing via voltammetry. Since the precursor to the CP is a small organic molecule (monomer), the chemical sensor moiety can be built into the monomer structure through synthetic methodologies, allowing the creation of electrode supported CP films that fall in a unique class of chemoselective sensors.

**Synthetic Methodologies**

Cross-coupling reactions are the most powerful tools for the synthesis of a wide array of CPs. The use of cross-coupling reactions results in a step-growth polymerization. The most common cross-coupling methods utilized in the synthesis of CPs include Kumada, Stille, Suzuki, and Heck reactions, all of which employ either a palladium or nickel catalyst. The catalytic cycle (Figure 1.2), which is generic for many cross-coupling methodologies, begins with oxidative addition, followed by transmetallation, and finally couples two species through reductive
elimination. In the *oxidative addition* step, a M(0) catalyst inserts into an aryl-halogen bond, producing an aryl-M(II)-X species, where X is a halogen and M is palladium or nickel. Upon insertion, the oxidation state of the metal increases from M(0) to M(II). The *transmetallation* step of the catalytic cycle is unique depending on the nucleophile type. In the case of Kumada type coupling, a Grignard nucleophile transmetallates with the aryl-M(II)-Br formed via the preceding oxidative addition step. The product of the transmetallation step is an unstable aryl-M(II)-aryl species, which quickly proceeds to reductive elimination. In *reductive elimination*, the M(II) catalyst couples the two aryl species, leaving an aryl-aryl dimer and eliminating M(0). The catalytic cycle is repeated.

![General catalytic cycle for cross-coupling reactions employing nickel or palladium catalysts.](image)

**Figure 1.2.** General catalytic cycle for cross-coupling reactions employing nickel or palladium catalysts.

In the synthesis of CPs, this type of condensation polymerization can follow a *step-growth* or *chain-growth* mechanism. In step growth, A-A and B-B type monomers are used. In such step growth polymerizations, any molecular species
can react with one another. Monomer can react with monomer to form a dimer, a
dimer may react with monomer to form a trimer, or a dimer can react with another
dimer to form a tetramer. Therefore, high molecular weight is achieved only at very
high monomer conversion. In a chain growth polymerization, monomer can only
react with a propagating polymer chain, and a single catalyst initiates a single chain.
Such chain-growth polymerizations employ a bifunctional A-B type monomer,
where both the aryl halogen electrophile and nucleophile are on the same molecule.
Through the use of such bifunctional monomers, cross-coupling can proceed by a
unique catalyst-transfer mechanism, yielding the chain-growth nature of the
polymerization. In the catalyst-transfer mechanism, the reductively eliminated M(0)
species undergoes intramolecular oxidative addition at the carbon-halogen bond of
the elongated polymer endgroup. This species then can undergo transmetallation
with another monomer. The propagating catalyst remains at the end of the polymer
chain throughout the polymerization due to the intramolecular catalyst-transfer
step at the elongated polymer end. A distinct advantage of this technique is that it
introduces the ability to obtain near monodisperse and regioregular polymers, to
prepare end-functionalized polymers, and to create a diverse array of block copolymers and macromolecular architectures. Such polymerizations are termed
catalyst-transfer polymerizations.

Prior to cross-coupling methodologies, a useful way to generate thin films of
CPs was through electrochemical polymerization. This method is used commonly
for the synthesis of poly(thiophene)s.\textsuperscript{17} In the proposed mechanism for five-
membered heterocycles,\textsuperscript{18} the first electrochemical step is the oxidation of
monomer to its radical cation, followed by the coupling of two radicals to produce a dihydridimer dication. After loss of two protons and rearomatization, the dimer then undergoes oxidation, which reacts with another monomeric radical. This process is repeated until the oligomer becomes insoluble and precipitates onto the electrode surface. In the case of the electrochemical synthesis of poly(3-alkylthiophenes)s (P3AT)s, random couplings are created, which result in regioirregular polymers (Figure 1.3). The loss of regioregularity is due to a combination of head-to-head and tail-to-tail couplings, which causes a twisting of the polymer backbone. This undesirable twisting of the backbone results in a loss of conjugation and degradation of the electronic properties of P3AT.

In 1992, McCullough and coworkers reported the first regioregular P3ATs by employing Kumada cross-coupling methods.\textsuperscript{19, 20} In this method, regiospecific generation of 2-bromo-5-bromomagnesio-3-alkylthiophene is achieved through treatment of 2-bromo-3-alkylthiophene with lithium diisopropylamide (LDA) at -78 °C, followed by quenching with magnesium bromide ethyl etherate (MgBr\textsubscript{2} Et\textsubscript{2}O). Polymerization was initiated \textit{in situ} by addition of a catalytic amount of Ni(dppp)Cl\textsubscript{2}. Two monomers undergo transmetallation with this catalytic species to generate the
actual polymerization “initiator”. Based on quenching studies, it was found that the resulting polymer was 98-100% regioregular and displayed $M_n$ values ranging from 20,000-40,000 g/mol with a polydispersity index (PDI) around 1.4. To avoid the use of cryogenic temperatures, the McCullough method was later improved to the Grignard Metathesis (GRIM) method.\textsuperscript{21, 22} In the GRIM method, 2,5-dibromo-3-alkylthiophene is treated with one equivalent of a Grignard reagent (RMgX) to form a mixture of intermediates, in which the magnesium halogen exchange takes place at either the 2- or 5-position in a ratio of 85:15 to 75:25, respectively. Although the ratio of undesirable isomers is higher than the McCullough method, P3AT’s with regioregularity of 99% or higher are still obtained. This can be attributed to the steric effect of aliphatic substituents \textit{ortho} to the nucleophile.\textsuperscript{23} Typical $M_n$ values of the polymers synthesized through the GRIM method are between 20,000-35,000 g/mol, with a PDI around 1.2-1.4. The Rieke method was also reported,\textsuperscript{24} where 2,5-dibromo-3-alkylthiophene was treated with highly reactive Rieke zinc. Such Rieke metals are highly reactive due to their large surface area and lack of a surface oxide layer.\textsuperscript{25} This zinc was found to react 2,5-dibromo-3-hexylthiophene with 90% regioselectivity. Polymers were obtained with a regioregularity greater than 97% and $M_n$ values around 24,000-34,000 g/mol using Ni(dppe)Cl$_2$.

Yokozawa\textsuperscript{26} originally proposed that this condensation reaction proceeds via a chain-growth mechanism, followed by McCullough, who in addition claimed that KCTP is a quasi-living system.\textsuperscript{27, 28} In the GRIM method, it was observed that P3ATs with relatively high molecular weight are produced early in the reaction, which contradicts a step growth mechanism. Also observed was that the $M_n$ values of the
polymers increased in proportion to monomer conversion, and was controlled by the amount of the nickel catalyst. Experiments to extend the “active” chain-end after monomer depletion were performed successfully, where addition of a new portion of monomer resulted in an increase of the molecular weight of the final polymer. This strategy was used to create a triblock copolymer poly(3-dodecylthiophene)-b-poly(thiophene)-b-poly(3-dodecylthiophene). Addition of various Grignard reagents to the nickel terminated P3AT resulted in the formation of end-functionalized polymers

![Diagram of the proposed mechanism of Kumada Catalyst-Transfer Polycondensation](image)

**Figure 1.4.** Proposed mechanism of Kumada Catalyst-Transfer Polycondensation according to McCullough and Yokozawa.

It is proposed that Kumada catalyst-transfer polymerization (KCTP) is initiated by double transmetallation of a Ni(II) species with an organometallic nucleophile (1), as illustrated in Figure 1.4. This process leads to a diorganonickel
intermediate, in which both compounds are σ-bound (2). The low stability of 2 leads to reductive elimination, giving a new C-C bond and a Ni(0) species (3). Bidentate ligands such as 1,2-bis(diphenylphosphino)ethane (dppe) or 1,2-bis(diphenylphosphino)propane (dppp) force the two σ-bound aryl species into a cis configuration around the metal center, giving the orientation that is necessary for reductive elimination. Upon reductive elimination, the Ni(0) catalyst is speculated to be coordinated to the ring system prior to sequential oxidative addition. Such coordination of Ni(0) centers to an aryl ring has been shown by theoretical studies and kinetic isotope effect experiments to be the first irreversible step in oxidative addition of Ni(0) to an Ar-X bond. If the product of the reductive elimination step has a sufficiently reactive halide substituent as in the case of (1), the ligated M(0) will selectively add to that Ar-X bond without being displaced from its coordination to the aromatic system, yielding (4). It is this coordination and subsequent oxidative addition that leads to the chain-growth character of KCTP.

**Developments**

A particularly useful modification of KCTP involves the use of an “external initiator,” in which the catalyst is added in the form of (Ph)Ni(II)L2-X. Such external initiators are synthesized and isolated prior to the polymerization. This is accomplished by oxidative addition of a Ni(0) catalyst to an aryl halide, or by transmetallation of an organolithium or organomagnesium species with a M(II) center (Figure 1.5). The polymer resulting from this process is functionalized at one end with the aromatic moiety derived from the external initiator. This strategy
has been implemented to prepare a wide variety of end-functionalized and surface-grafted CPs.\textsuperscript{35,36,39,40}

\[
\begin{align*}
\text{Ph-Br} & \quad \xrightarrow{\text{Ni(0)L}_4} \quad \text{Ph-Ni(II)L}_2\text{-Br} \\
\text{Ph-Li} & \quad \xrightarrow{\text{Ni(II)L}_2\text{X}_2} \quad \text{Ph-Ni(II)L}_2\text{-X}
\end{align*}
\]

\textbf{Figure 1.5.} Formation of an external initiator using a Ni(0) catalyst.

The external initiation of KCTP to form poly(3-hexylthiophene) (P3HT) was first carried out by Senkovskyy \textit{et al.}, where phenyl-terminated P3HT was synthesized from (Ph)Ni(PPh\textsubscript{3})\textsubscript{2}Br.\textsuperscript{34} According to MALDI-TOF data, 80\% of the externally initiated P3HT is terminated by a phenyl group on one end and by either a hydrogen or bromine atom at the other. This along with other evidence suggests that externally initiated P3HT with monodentate PPh\textsubscript{3} ligands follows a chain-growth mechanism. The observed polymers had molecular weights of 4,100 g/mol, which is much lower than typically used for electronic applications. The low molecular weight can be attributed to chain-termination processes inherent in the use of monodentate phosphine ligands. To acquire further control of the polymerization, bidentate ligands must be employed.

The employment of bidentate ligands in externally initiated P3HT was done by the Luscombe group.\textsuperscript{23} Neat o-tolyl chlorides were reacted with Ni(PPh\textsubscript{3})\textsubscript{4} to form the monodentate ligated \textit{trans}-chloro(o-tolyl)bis(triphenylphosphine)nickel(II) complex. Addition of excess dppp to this complex formed the thermodynamically favored bidentate ligated \textit{cis}-chloro(o-tolyl)(dppp)nickel(II) complex, which was characterized using $^{31}$P NMR.
resulting external initiator was then used to make fully regioregular poly(3-hexylthiophene) all in a single pot. This system outperformed previous studies,\textsuperscript{34} with molecular weights reaching 9.8 kDa with a PDI of 1.2. Complete introduction of the \(o\)-tolyl end groups was observed via integration of \(^1\text{H}\)-NMR signals. The Luscombe group also experimented with different external initiator structures, in which aryl halides with various substituents on the phenyl ring were reacted with Ni(PPh\(_3\))\(_4\).\textsuperscript{35} Highly electron-rich aryl halides bearing \(\pi\)-donor substituents such as 4-bromomethoxybenzene failed to initiate polymerization.

Kiriy and coworkers, through the use of external initiators, studied the nature of the intramolecular catalyst-transfer step in KCTP.\textsuperscript{41} It is known that the observed intramolecular catalyst-transfer in KCTP is a result of Ni(0) complexes that preferentially coordinate to aromatic \(\pi\)-systems. Initially, the Kiriy group observed that the intramolecular catalyst-transfer step is robust, even for monomers comprised of three thiophene units (terthiophenes), giving a ring walking distance of 1.17 nm.\textsuperscript{41} At the time, it was not clear whether the migration of Ni(0) along the growing polymer chain was unidirectional or bidirectional. It was presumed that upon the reductive elimination step, the Ni(0) catalyst can coordinate to the \(\pi\)-system on either side of the newly formed carbon-carbon bond. To investigate the mobility of the coordinated Ni(0) species, the Kiriy and coworkers utilized Br-C\(_6\)H\(_4\)-Ni(dppe)-Br external initiators, where the position of the phenyl type initiating species in the final P3HT backbone could be easily determined using NMR.\textsuperscript{42} The presence of the additional bromine group on the external initiator can facilitate bidirectional polymerization. Upon isolation of the
polymeric product, if the initiating species is located inside the chain (a phenyl unit), then random bidirectional ring walking has occurred. If the initiating species is located at the end of the chain (a p-bromophenyl unit), then unidirectional ring walking has occurred. It was found that the polymeric product containing the initiator inside the chain accumulates as the DP increases. The major product is the polymer with the initiator located at the chain-end, which leads to the observation that the coordinated Ni(0) has a higher affinity for thiophene units over phenyl units. Remarkably, the fact that the amount of polymer with the initiator inside the chain continues to increase at relatively high DPs suggests that the Ni(0) catalyst is capable of ring walking over distances of several tens of nanometers.

**Surface modification with Conjugated Polymers**

Processing soluble CPs from solution has disadvantages in current device architectures, especially when multiple layers of material must be printed on top of one another. The processing that can be performed upon cast films of polymer is severely limited, as most solvents will cause swelling, reorganization of polymer chains, and even delamination of a film that is not covalently bound. In addition to solvent processing conditions, cast films of polymer are also susceptible to degradation by physical processes of abrasion, thermal expansion and contraction, and stress from bending. It is therefore highly desirable in certain applications for the polymers to be permanently (irreversibly) immobilized to the surface.
Figure 1.6. Illustration of the different polymer grafting regimes. Reproduced with permission from Ref 26.

Three approaches exist for the modification of surfaces with polymer layers (Figure 1.6). The first approach involves a *grafting-to* process, where a polymer is synthesized in solution that either possesses functionality at one end due to the polymerization technique, or which has been end-functionalized post-polymerization through some chemical transformation. This end-group is then reacted with a second, complementary functional group on the surface. This strategy has been recently illustrated by the Gopalan group, who used ethynyl-terminated poly(3-hexylthiophene) to react with azide-functionalized surfaces through Cu(I)-catalyzed Huisgen 1,3-dipolar cycloaddition.\(^{43}\) This technique has the advantage of simplicity, but has a major fundamental limitation in that polymer grafting density is limited both thermodynamically and kinetically.\(^{44}\) Polymer chains remain in their entropically favored random coil configuration before and after
surface immobilization. The forms a blocking layer at the interface to other nearby reactive sites. Such non-interacting random coils tethered to the interface are referred to as the “mushroom regime”. In good solvents, the thickness of immobilized polymer coils is proportional to the degree of polymerization. For these reasons, only very low film thickness values are obtained using this approach.

The second approach is a *grafting-from* process, which relies on the immobilization of an initiator at a surface through chemical self-assembly, followed by the reaction of this surface-bound species with monomer in solution. This process can lead to covalently immobilized CPs at high grafting densities. The distance between grafted polymer chains is typically much less than the size of the polymer coil, or Flory radius. This configuration is known as the “brush regime”. Due to excluded volume effects, the polymer chain will forcibly grow in a more extended conformation throughout the surface-initiated polymerization. While this extended conformation has entropic energy loss, the stretched chains can interact more collectively. In this geometry, conformational changes using stimuli such as temperature or polymer solvation, can dramatically alter film properties such as thickness and morphology. This surface-initiated polymerization (SIP) method has several limitations: (1) it is limited to chain-growth polymerizations, (2) requires the often-difficult step of initiator immobilization at the surface, and (3) generally involves a more complex experimental setup than other approaches with separate steps of initiator immobilization and the polymerization reaction. Polymerizations which are *living or controlled* in solution - that is, which have low chain transfer and termination rates compared to the rate of polymerization - are often adapted for the
grafting-from preparation of polymer brushes. The use of such living or controlled polymerizations allow for one to maintain a reactive chain end during the course of the polymerization. Examples of polymerizations which have been adapted for the production of polymer brushes include (but are not limited to) atom transfer radical polymerization and nitroxide mediated radical polymerization,\textsuperscript{46} and ring opening metathesis polymerization.\textsuperscript{47}

An intermediate approach, \textit{grafting-through} polymerization, involves simply performing a solution polymerization in the presence of a surface functionalized with groups which react in the polymerization.\textsuperscript{48} This method is conceptually simple and allows for a one-pot process of synthesis and immobilization of the polymer. In a few cases, grafting-through polymerization has achieved high grafting densities of polymer, only under such conditions where the surface-bound polymer layer grows evenly during the course of the polymerization.\textsuperscript{48-51} However, grafting through polymerization does not achieve the grafting densities obtained using grafting from.

It is important to recognize the inherent difficulties associated with the low solubility of conjugated polymers in the preparation of covalently bound CP films. These materials are intractable because of their complete insolubility and infusibility. Therefore, for unsubstituted CPs, \textit{in situ} polymerization techniques are required for the formation of covalently bound films. Even CPs solubilized by modification with alkyl chains have strong intermolecular forces and tend to aggregate, particularly in less polarizable solvents. These tendencies strongly affect the ability of CP chains in solution to react at a surface, due to the kinetic unfavorability of reaction for surface-bound active sites near aggregates on the
surface. For these reasons, recent work on forming covalently grafted CP films has focused on surface-directed polymerization.

**Objectives and Outline of this Dissertation**

In this dissertation, Kumada Catalyst-Transfer Polycondensation is utilized in a *grafting-from* approach to generate surface-bound CPs on a variety of substrate types. Such covalently immobilized films can give rise to very unique systems that can be used for a variety of applications in photovoltaics and organic electronics. Additionally, the interaction of conjugated polymer chains with one another in close proximity can lead to orientation of polymer chains near parallel to the surface normal. Such architecture can lead to interesting optical properties.

In addition to the characterization of fabricated conjugated polymer films, much research in this dissertation is focused on understanding the role of nickel catalysts at the interface. It is this area that required the most attention in adapting this new polymerization methodology to work from surfaces. When active chain-ends or initiators are in close proximity to one another, they undergo unwanted side reactions, leading to termination of the polymerization.

Chapter 2 of this dissertation describes a novel technique in the fabrication of poly(thiophene) and poly(phenylene) thin films using surface-initiated Kumada catalyst-transfer polycondensation. The resulting films are characterized by ellipsometry, UV-VIS, fluorescence microscopy, electrochemistry, and PM-IRRAS. This chapter was highlighted in Chemical Science and described as “The skyscraper approach to nanoelectronics”.

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Chapter 3 of this dissertation investigates in further detail the nature of nickel-mediated reactions at the interface. The behavior of Ni(II) species in close proximity is observed to be dependent on the nickel-ligand environment and initiator structure. In addition, ultra uniform poly(3-methylthiophene) thin films are fabricated from a variety of initiating species using the Kumada catalyst-transfer polycondensation technique. This chapter has provided further insight into the behavior of Ni(II) species, allowing for a more rational design of surface-bound initiators.

Chapter 4 utilizes the kinetic isotope effect (KIE) to investigate Ni(0) interactions with haloarenes. A series of Grignard reactions are carried out with bromotoluene, chlorotoluene, and bromothiophene derivatives. Through systematic variation of the substituent location on the ring or the halide type, it was observed that the first irreversible step (FIS) of Ni(0) oxidative addition changes. The results in this chapter further explain the interfacial behavior of Ni(II) species observed in Chapter 3.

Chapter 5 summarizes the chapters of this dissertation and also provides an outlook as to how this dissertation will impact future studies.
References


CHAPTER 2

FORMATION OF CONJUGATED POLYMER BRUSHES BY SURFACE-INITIATED CATALYST-TRANSFER POLYCONDENSATION

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Abstract

Electroactive conjugated polymer brushes of poly(thiophene) and poly(phenylene) have been prepared via a surface-initiated Kumada-type polycondensation (SI-KCTP) reaction, yielding films with a thickness up to 42 nm. The resulting films are extensively characterized using PM-IRRAS, cyclic voltammetry, and ellipsometry. This is a first report of an electroactive polymer film covalently immobilized to an electrode using the SI-KCTP reaction.
Introduction

Conjugated polymers have attracted much interest as a promising new class of materials, with applications in solar cells, LEDs, memory, and sensors. As more complex device architectures are created, it becomes increasingly important to develop techniques to interface these materials with traditional electronic components made of metal or conducting oxide. Furthermore, this need is especially apparent in the field of nanotechnology, where methods to connect macroscopic electrodes to molecules or nanoscale objects (“molecular junctions”) are sought as lithography is pushed to its theoretical limit. For these reasons as well as others, methods for forming covalently attached conductive polymer layers on metal or conducting oxide are highly desirable. Unfortunately, few such methods exist.\(^1\)-\(^3\)

Direct electropolymerization of a conjugated monomer from an electrolyte solution is the most common and versatile technique available at present. While this technique is simple in execution, allows for control of film thickness by varying the time and oxidation potential, and can be used on a variety of monomers, it tends to produce insoluble films with highly irregular morphologies as well as regioirregular polymers. These drawbacks signify the need for a more versatile approach that affords better control of electronic properties and ultimately, molecular architecture.

The recent development of catalyst-transfer polycondensation polymerization using metal-mediated coupling reactions on bifunctional, A-B type monomers by the Yokozawa group\(^4\)-\(^6\) has been used by Kiriy et al. to prepare well-defined graft copolymer films, in which the grafted block is not only conjugated, but
nearly monodisperse. The controlled and near-living nature of this polymerization proceeds by a chain-growth mechanism due to a unique intramolecular catalyst-transfer step. This work is an improvement over step-growth methodologies, in which the polymerization of conjugated monomers from polymer-bound initiators proceeds in an uncontrollable fashion. Attempts to grow conducting polymer brushes from a monolayer using the Kumada catalyst-transfer polycondensation strategy have previously failed due presumably to early chain-termination processes. Recently, an alternative methodology based on palladium-catalyzed Suzuki polycondensation was used to grow polyfluorene films with thicknesses up to 100 nm.

**Figure 2.1.** Preparation of conjugated polymer brushes using catalyst transfer condensation polymerization from a surface bound Ni coupling catalyst.
In this report, we have adapted the Kumada-type catalyst-transfer polycondensation to the formation of electroactive conjugated polymer brushes directly from surface-bound initiators (Figure 2.1). The use of arylmagnesium precursors are straightforward to prepare, use inexpensive starting materials, and are amenable to thiophene-based monomers, which proceed much more sluggishly with Suzuki coupling due to difficulties with deboronation of the thiophene boronic acids or esters during polymerization and sluggish oxidative addition of the palladium catalyst to the electron rich thiophene ring.12,13

Experimental

Ellipsometry. Ellipsometric measurements were performed on a Multiskop (Optrel GbR) with a 632.8 nm HeNe laser light source. Thickness data for films were obtained by fitting ellipsometric data using integrated specialized software. Measurements given are the average of three or more data points.

PM-IRRAS measurements. All PM-IRRAS measurements were made on a Nicolet Model 6700 spectrometer equipped with a photoelastic modulation (PEM) accessory (ThermoNicolet, Madison, WI) using OMNIC 8.0 software. All measurements were made with the grazing angle set at 80 degrees.

Cyclic voltammetry measurements. All electrochemical measurements were made using a CH Instruments CHI832B bipotentiostat. Unless otherwise indicated, electrochemical experiments were performed using 0.1M tetrabutylammonium hexafluorophosphate as the supporting electrolyte in DCM or THF and taken vs. a Ag/Ag+ pseudoreference electrode with Fc/Fc+ used as an internal standard (0.414 V/SCE). Potentials reported in this solvent system are given vs. SCE.
Electrochemistry of PPh brushes was performed in 95% H₂SO₄ and potentials are given directly vs. an Ag/Ag⁺ pseudoreference electrode. The area of the working electrode immersed in the electrolyte solution was kept at approximately 1 cm x 1 cm for all samples.

**Atomic Force Microscopy.** The AFM topography images of the films were recorded in tapping mode using a Multimode NanoScope IIIa (Digital Instruments/Veeco Metrology Group) at a scan rate of 1 Hz and tip velocity of 2 um/sec. Silicon AFM probes with a resonant frequency of 300 kHz, spring constant of 40 N/m, and tip radius of <10 nm were used. In all AFM images, differences in height are indicated by color: white is the highest and dark is the lowest.

**Materials.** Solvents and reagents were obtained from TCI or Sigma-Aldrich unless otherwise indicated. Solvents used were purified by distillation from calcium hydride (toluene, methylene chloride) or sodium ketyl (THF), and sparged with argon gas to remove oxygen before use in the glove box.

**Synthesis of initiator 6-(5-bromothiophen-2-yl)hexane-1-thiol.** 23.8 ml of n-butyl lithium (2.5 M in hexane, 59.4 mmol) was added dropwise to a solution of thiophene (5 g, 59.4 mmol) in 50 ml of THF at -78 °C under N₂ via syringe. After 45 min., the mixture was transferred dropwise to another flask containing 1,6-dibromohexane (36.23 g, 148.5 mmol) in 100 ml of THF. After complete addition, the mixture was warmed to room temperature overnight. The solution was then poured into ice water, extracted with methylene chloride, and dried over MgSO₄. After distillation, the product was purified by flash chromatography using hexanes as the eluent to yield 10.44 g (71%) pure liquid 2-(6-bromo-hexyl)-thiophene. ¹H
NMR (300 MHz, CDCl₃); δ 7.10 (dd, 1H, J = 5.1, 1.2 Hz), 6.91 (dd, 1H, J = 5.1, 3.5 Hz), 6.77 (dd, 1H, J = 3.5, 1.2 Hz), 3.40 (t, 2H, J = 6.8 Hz), 2.83 (t, 2H, J = 7.5, 15.1 Hz), 1.87 (m, 2H), 1.70 (m, 2H), 1.45 (m, 4H). NBS (8.3 g, 46.6 mmol) in DMF was added dropwise to a solution of 2-(6-bromo-hexyl)-thiophene (10.44 g, 42.4 mmol) in 15 ml of DMF under darkness. After stirring overnight, the mixture was poured into ice water and extracted with methylene chloride, dried with MgSO₄, and purified by flash chromatography using hexanes as the eluent, which afforded 8.62 g (62.3%) 2-bromo-5-(6-bromo-hexyl)-thiophene. ¹H NMR (300 MHz, CDCl₃); δ 6.84 (d, 1H, J = 3.5 Hz), 6.53 (d, 1H, J = 3.5 Hz), 3.40 (t, 2H, J = 7.0 Hz), 2.75 (t, 2H, J = 7.7 Hz), 1.86 (m, 2H), 1.65 (m, 2H), 1.42 (m, 4H). To a solution of 2-bromo-5-(6-bromo-hexyl)-thiophene (.86 g, 2.60 mmol) in 5 ml THF at -10 °C was added hexamethyltrisilathiane (.56 g, 3.1 mmol) and TBAF (2.9 ml, 1.0 M in THF). TLC indicated completion after overnight stirring, and the mixture was diluted with diethyl ether and washed with aqueous ammonium chloride (sat.). Purification of the thiol was obtained by flash chromatography using 1:9 DCM:hexane, which yielded 0.10 g (11.6%) 6-(5-bromothiophen-2-yl)hexane-1-thiol. ¹H NMR (300 MHz, CDCl₃); δ 6.83 (d, 1H, J = 3.5 Hz), 6.52 (dt, 1H, J = 3.5, .9 Hz), 2.74 (t, 2H, J = 7.5 Hz), 2.51 (q, 2H, J = 7.5 Hz), 1.62 (m, 4H) 1.39 (m, 5H). ¹³C NMR (300 MHz, CDCl₃); δ 131.90, 129.45, 124.55, 108.66, 33.72, 31.26, 30.10, 28.23, 27.94, 24.47.

**Synthesis of 2,5-diiodothiophene.** 49.9 mL of nBuLi (2.5 M, 124.7 mmol) was added to a solution of thiophene (5 g, 59.4 mmol) and TMEDA (18.6 mL, 124.7 mmol) in THF (60 mL). After 1 h of stirring, iodine (31.6 g, 124.7 mmol) dissolved in 30 mL of THF was added dropwise. The solution was allowed to stir overnight. A
small amount of 2-iodothiophene was distilled off under reduced pressure, and the dark brown residue was purified by flash chromatography using hexanes as the eluent, which yielded 4 g (20 %) of 2,5-diiodothiophene as a yellow-orange oil. $^1$H NMR (300 MHz, CDCl$_3$); $\delta$ 6.93 (s, 2H).

**Formation of gold substrates.** Glass slides (VWR VistaVision microscope slides) were cleaned by sonicating in isopropanol for 15 min. Slides were dried under an argon stream and placed immediately in a thermal evaporator (Thermionics Northwest model SMR-4R). 10 nm of chromium was evaporated at a deposition rate of 0.1 Å/sec, followed by 100 nm of gold at a deposition rate of 0.5 Å/sec.

**Formation of monolayers.** Gold substrates (100 nm Au/10 nm Cr) were cut in rectangular pieces of approximate dimensions 2.5 x 1 cm, placed directly into a 2 mmol solution of thiol initiator (6-(5-bromothiophen-2-yl)hexane-1-thiol) in toluene, and incubated for 12-24 h.

**Formation of aryl A-B monomers.** 2,5-dibromothiophene, (TCI) 1,4-diiodobenzene, (Eastman) or 2,5-diiodothiophene (1 mmol) was dissolved in anhydrous THF (10 mL) in a Schlenk flask under nitrogen. The temperature was lowered to 0 °C degrees in an ice bath, and isopropylmagnesium chloride 2.0 M (0.45 mL, 0.9 mmol) was added dropwise and stirred for 1 h. The solution was allowed to come to room temperature, sealed, and transferred to the glove box.

**Formation of brushes.** Gold substrates functionalized with thienyl bromide monolayer were placed for 3 h in a 0.05 wt % Ni(COD)$_2$ + 4PPh$_3$ solution, prepared by adding 10 mL toluene to 5 mg Ni(COD)$_2$ and 19 mg PPh$_3$ immediately before the solution was to be used. Substrates were then removed from this solution, rinsed
thoroughly with toluene and THF, and placed in monomer solution overnight. All polymerizations were carried out at room temperature in a glovebox. The polymer-grafted substrates were then removed from the glovebox and rinsed with 1M HCl, water, chloroform, and sonicated briefly in THF. In the case of PPh, the same procedure was carried out with a gold substrate functionalized with a monolayer of 11-undecanethiol as a control experiment. Some polymer formed on the control slide, presumably due to physisorption of polymer from solution; however, the control film was distinguishable from the polymer brush in that it was far thinner, rougher, and delaminated extensively under a Scotch tape peel while the PPh brush remained unchanged.

**Discussion and Results**

To this end, we have fabricated gold surfaces functionalized with monolayers of an aryl bromide moiety that undergoes oxidative addition when placed in a solution of a reactive Ni(0) species to produce a surface-bound metal-mediated coupling catalyst. We have successfully polymerized two A-B type monomers from the surface-bound catalyst in a surface-initiated Kumada catalyst-transfer polycondensation (SI-KCTP). To our knowledge, this is the first report of an electroactive conjugated polymer formed directly from a monolayer using the Kumada-type catalyst-transfer chain-growth technique.

We have used Grignard-stable MgCl-Ar-I type AB monomers to produce brushes of poly(thiophene) (PT) and poly(p-phenylene) (PPh), two widely used conducting polymers. The Ni(0) complex used to prepare the surface-bound metal-mediated coupling catalyst is formed by the addition of four equivalents of
triphenylphosphine to a 0.05 wt% solution of Ni(COD)₂. This solution turns a dark red color upon formation, presumably by the dissociation of a 1,5-cyclooctadiene (COD) ligand to form the more reactive Ni(COD)(PPh₃)₂ complex. We have found that the use of this solution results in the growth of polymer brushes, while Ni(PPh₃)₄ does not. The lower reactivity of the coordinately saturated Ni(PPh₃)₄ has also been observed in the synthesis of polythiophenes.¹⁴ While Ni(PPh₃)₄ adds to aryl bromides in solution on the order of hours at room temperature, we observed rapid precipitation of a ArNi(II)Br complex upon addition of 2-bromothiophene to a solution of the Ni(COD)(PPh₃)₂.

![Cyclic voltammetry of the surface-bound ArNi(II)Br complex](image.png)

**Figure 2.2.** CV displaying the presence of Ni(II) at the interface using Ni(COD)(PPh₃)₂ (black line) and Ni(PPh₃)₄ (red line).

Cyclic voltammetry of the surface-bound ArNi(II)Br complex (Figure 2.1) is shown in Figure 2.2. An irreversible oxidation of a nickel(II) species is observed at 0.67 V/SCE, consistent with solution voltammetry performed on similar systems.¹⁵
Further cycles did not reproduce the oxidation wave. In addition, using Ni(PPh$_3$)$_4$ as the catalyst, we observe a different initiating species, as seen by a shift in the oxidation potential in Figure 2.2. We have also observed that the Ni(0) catalyst adds more efficiently to monolayers containing a thienyl bromide moiety than to oxyphenyl bromide monolayers. Once the catalyst is generated on the surface by immersing a substrate with a suitable monolayer in the reactive Ni(0) solution for at least 3 h, the substrates are then removed and thoroughly rinsed before immersing in a solution of monomer, formed by magnesiation of a suitable aryl dihalide with isopropylmagnesium chloride. Brushes with a thickness of 10-42 nm have been formed with a variety of aryl Grignard reagents.

**Table 2.1.** Polymer brushes synthesized and their corresponding thickness values. The control substrate demonstrated far thinner polymer layers, which was easily delaminated via sonication in chloroform.

<table>
<thead>
<tr>
<th>Brush</th>
<th>Thickness (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Poly(thiophene) from Br-T-MgCl</td>
<td>10 nm</td>
</tr>
<tr>
<td>Poly(thiophene) from I-T-MgCl</td>
<td>14 nm ±2 nm</td>
</tr>
<tr>
<td>Poly(thiophene) from I-T-MgCl</td>
<td>36 nm</td>
</tr>
<tr>
<td>Poly(phenylene) from I-Ph-MgCl</td>
<td>42 nm ±3 nm</td>
</tr>
<tr>
<td>Poly(phenylene) control slide</td>
<td>19 nm ±7 nm</td>
</tr>
</tbody>
</table>
Figure 2.3. CV of a poly(thiophene) brush (bottom) and a poly(phenylene) brush (top). Scan rate = 50 mV/s. Inset: Anodic and cathodic peak currents vs. scan rate.

After the polymerization, a small amount of polymer is generally observed in solution. The unattached polymer is likely due to the nickel species undergoing chain transfer off the surface by one of two processes; oxidative addition to the aryl halogen of an A-B type monomer in solution, leaving behind a chain on the surface terminated with an aryl bromide moiety, or transmetallation with an unreacted iPrMgCl unit, which terminates the chain with an isopropyl group. Based upon reports of decreased polydispersity with low temperature in similar systems, it is probable that chain transfer due to the first process could be limited by reducing the
polymerization temperature. The second process likely contributes as well, since all polymers prepared by this method have had faint methyl C-H signals in their infrared spectra at 2957 cm$^{-1}$, and preparation of the monomer solution with 0.9 eq. of $i$PrMgCl yields thicker films than use of 1.0 eq. of the Grignard. An optimization of the conditions for polymerization and an investigation of the kinetics of brush growth are underway in our laboratory.

![PM-IRRAS spectra](image)

**Figure 2.4.** PM-IRRAS spectra of a poly(phenylene) brush (top) and a poly(thiophene) brush (bottom). The C-H stretching region of PPh is scaled by a factor of 10.
We have characterized the resulting surface-bound conjugated polymers via cyclic voltammetry (CV). Figure 2.3 shows the CV of a 14 nm PT and a 42 nm PPh brush grown using our technique. In PT, an anodic current peak (E_{pa}) occurs at 0.86 V/SCE. The oxidation prewave occurs ca. 0.3 V/SCE, consistent with electropolymerized films of polythiophenes. The PPh film displays intense doping/dedoping waves in concentrated H_2SO_4. The inset for both voltammograms shows anodic peak current as a function of scan rate, which displays the linearity expected of a species covalently bound to an electrode.

In addition to CV, the resulting films have also been analyzed by polarization-modulation infrared reflection absorption spectroscopy (PM-IRRAS) and atomic force microscopy (AFM), and PPh by fluorescence microscopy. Figure 2.4 shows the PM-IRRAS spectrum of the polymers shown in Figure 2.1. PT has a single and narrow aromatic C-H stretch at 3063 cm\(^{-1}\). Asymmetric C=C-H stretching occurs at 1516 cm\(^{-1}\) and 1490 cm\(^{-1}\), with the symmetric stretch occurring at 1457 cm\(^{-1}\). Out of plane C-H bending occurs at 792 cm\(^{-1}\). The C-S ring deformation can be observed at 768 cm\(^{-1}\). The aromatic C-H stretch of PPh is also visible, with a sharp peak at 3036 cm\(^{-1}\) and a shoulder at 3065 cm\(^{-1}\). Asymmetric C=C ring modes are assigned to 1515 cm\(^{-1}\) and 1480 cm\(^{-1}\), aromatic C-H in-plane bending at 1001 cm\(^{-1}\), and the strong singlet at 810 cm\(^{-1}\) characteristic of regioregular p-phenylene. The spectra match well with literature reports of electropolymerized films of PT and PPh. The fluorescence micrograph of PPh in Figure 2.5 shows its distinctive blue fluorescence.
**Figure 2.5.** Fluorescence microscopy image of bare Au (top) and 42 nm PPh brush on Au (bottom), displaying the characteristic blue fluorescence.

A representative morphology of the SI-KCTP formed films on gold is shown in Figure 2.6. The PT film shows a uniform and globular morphology with an RMS roughness of 3.9 nm. The films are considerably smoother than the underlying gold substrate prepared by thermal evaporation, which has an RMS roughness of 11.9 nm. PPh is shown in Figure 2.7.

**Figure 2.6.** Tapping mode AFM image of a poly(thiophene) brush prepared using SI-KCTP.
Figure 2.7. Tapping mode AFM image of a poly(phenylene) brush prepared using SI-KCTP.

Conclusion

In summary, we have developed a technique for performing Kumada-type catalyst-transfer polymerization from aryl-halide containing self-assembled monolayers, and used it to prepare a variety of conjugated polymer brushes. Further work will focus on the kinetics of polymer growth, chain orientation, and limiting chain transfer from the surface, which should yield the ability to “dial in” in a conjugated polymer brush of any desired thickness, as well as the formation of block copolymer brushes.
References


CHAPTER 3

SURFACE-CONFINED NICKEL MEDIATED CROSS-COUPLING REACTIONS:

CHARACTERIZATION OF INITIATOR ENVIRONMENT IN KUMADA CATALYST-TRANSFER POLYCONDENSATION

\[ \text{Eq. 1} \]

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Abstract

Kumada catalyst-transfer polycondensation (KCTP) has proven to be an excellent strategy toward the synthesis of well-defined conjugated polymers. In this report, Ni(0) species are reacted with surface-bound aryl bromides to yield KCTP initiators of structure (aryl)Ni(II)-Br. Surface-confined Kumada reactions are carried out with a ferrocene functionalized Grignard reagent to quantify initiator coverage, ligand exchange, and Kumada reaction kinetics. In addition, surface-initiated Kumada catalyst-transfer polycondensation (SI-KCTP) is carried out from the fabricated initiators to modify SiO₂ and ITO surfaces. Uniform poly(3-methylthiophene) films with thicknesses between 40 and 65 nm were characterized using a variety of spectroscopic and electrochemical techniques.
Introduction

Conjugated polymers (CPs) are an important class of materials that have recently attracted significant attention due to their potential in solar cells, fuel cells, sensors, and other organic electronic devices.\textsuperscript{1-3} In the context of thin film devices, the performance of the active layer is highly dependent on the organization, orientation, and crystallization of the individual CP chains.\textsuperscript{4} For example, dense surface immobilization of CPs in their uncoiled state may give rise to interesting optical and electronic properties. In addition, covalent attachment of conjugated molecules to conductive substrates (i.e. indium tin oxide (ITO)) can form an optimized interface for bulk heterojunction solar cells.\textsuperscript{5, 6} The nature of the connection between the ITO electrode and active organic layer has a large influence on device performance.\textsuperscript{7} Currently, poly(ethylenedioxy thiophene):poly(styrenesulfonic acid) (PEDOT:PSS) has become the standard material for increasing the work function of ITO for effective hole collection. A number of drawbacks exist with this approach: (1) the acidic nature of PEDOT:PSS tends to corrode the ITO electrode,\textsuperscript{8, 9} leading to a chemical instability at the interface,\textsuperscript{6} (2) the inhomogeneous conductivity of PEDOT:PSS leads to uneven charge extraction,\textsuperscript{10, 11} and (3) PEDOT:PSS does not have sufficient electron blocking capability,\textsuperscript{9, 12, 13} which could render charge recombination at this interface to reduce the short circuit current density ($J_{SC}$). The advantage of PEDOT:PSS is its insolubility in organic solvents, thus allowing for a secondary solution processing of organosoluble CPs without delamination or mixing with the underlying PEDOT:PSS layer. On the other hand, surface-initiated polymerization techniques offer a number
of unique advantages over physical deposition techniques, such as covalent immobilization of the polymer to the substrate, ability to prepare uniform coatings on objects of complex geometry, and ability to control grafting density based on initiator surface coverage.\textsuperscript{14, 15} The covalent immobilization of CPs to conductive substrates not only prevents delamination, but also allows additional versatility towards depositing an additional layer with similar solubility characteristics.

Conjugated polymers are fabricated using metal-mediated coupling reactions, which result in a condensation-type polymerization.\textsuperscript{16} The Kumada coupling reaction has received significant attention over the last decade, primarily due to the observation by McCullough and Yokozawa that the polymerization of 5-chloromagnesio-2-bromo-3-hexylthiophene follows a chain growth mechanism.\textsuperscript{17, 18} This polymerization, called Kumada catalyst-transfer polycondensation (KCTP), utilizes bifunctional AB-type monomers, which contain both a nucleophile and an aryl-halogen electrophile. The classic method of synthesizing CPs using KCTP involves a “one pot” initiation of the polymerization by adding a catalytic amount of Ni(dppp)Cl\textsubscript{2} (dppp = diphenylphosphino propane) or Ni(dppe)Cl\textsubscript{2} (dppe = diphenylphosphino ethane).\textsuperscript{16} The active Ni(0) catalyst is formed after a double transmetallation step. Senkovskyy \textit{et al.} later introduced external initiation of KCTP, where the active Ni(II) initiator was synthesized in a separate step before introduction to monomer.\textsuperscript{19} In this first report, poly(3-hexylthiophene) (P3HT) was initiated from (Ph)Ni(PPh\textsubscript{3})\textsubscript{2}Br, which was formed through the reaction of phenyl bromide with Ni(PPh\textsubscript{3})\textsubscript{4}, to create phenyl-terminated P3HT. Surface-initiated polymerization (SI-KCTP) was also demonstrated from immobilized poly(4-
bromostyrene) macroinitiators, which was later accomplished from covalently bound monolayers by our group.\textsuperscript{20, 21} In the context of surface coupling reactions, KCTP affords some inherent limitations including chemical compatibility of the monolayer interface with powerful Grignard reagents, amplification of steric effects due to the two-dimensional nature of the interface, restricted geometrical motions of the surface-confined molecules, and unwanted side reactions due to the close proximity of neighboring molecules.\textsuperscript{22-24}

In this report, different routes toward forming SI-KCTP initiators are investigated in terms of initiator density, homogeneity, and stability. A reactive cyclooctadiene nickel(0) (Ni(COD)\textsubscript{2}) complex was used as the precursor to a wide variety of Ni(0) complexes because of its inexpensive cost, commercial availability, and the facile dissociation of η-bound cyclooctadiene (COD) in the presence of σ-donating ligands. A variety of Ni(COD)\textsubscript{2}/ligand combinations are investigated in terms of combinations that yield the highest density and most homogeneous distribution of Ni(II) species at the interface. The resulting initiators are used to fabricate poly(3-methylthiophene) films using SI-KCTP.

**Experimental**

**Materials.** Isopropylmagnesium chloride solution (2.0 M in THF), nBuLi (1.6 M in hexanes), ferrocene, and bis(cyclooctadiene)nickel(0) were obtained from Acros Organics. Isopropylmagnesium chloride-LiCl (1.3 M in THF), 2,5-dibromothiophene, thiourea, sodium hydroxide, 3-methylthiophene, iodobenzene diacetate, triethyl phosphite, bromotrimethyl silane, sodium borohydride (NaBH\textsubscript{4}), aluminum chloride (AlCl\textsubscript{3}), 1,8-dibromooctane, thionyl chloride (SOCl\textsubscript{2}),
diisopropylamine, tetrahydrofuran (THF), toluene, dimethylformamide (DMF),
dichloromethane, hexanes, isopropyl alcohol (IPA), methanol, and glass slides were obtained from VWR. Gold substrates were obtained from EMF corp., (Ithaca, NY). Silicon wafers were obtained from University Wafer (South Boston, MA). Indium tin oxide (ITO) substrates were obtained from Thin Film Devices (Anaheim, CA). Toluene and THF were distilled from sodium ketyl and degassed by sparging with argon before use. Dichloromethane was distilled from CaH₂. Unless indicated otherwise, materials were used as received.

**Synthetic Methodology.** All synthesis was carried out under an inert atmosphere of purified argon or nitrogen, using standard Schlenk techniques or a glovebox (Unilab BP with an MB10 purification system, MBraun, Inc.). NMR spectra were recorded using a Varian Mercury 300 NMR spectrometer working at 300 MHz. Chemical shifts are reported relative to an internal tetramethylsilane standard.

![Figure 3.1](image_url)

**Figure 3.1.** Synthetic route to 2-ferrocenyl-5-bromothiophene. a) isopropyl magnesium chloride, CO₂, HCl. b) thionyl chloride. c) ferrocene, AlCl₃. d) NaBH₄, AlCl₃, reflux

**2-ferrocenyl-5-bromothiophene (Figure 3.1).** To a nitrogen-purged 250 mL 3-neck flask was added 2,5-dibromothiophene (5 g, 20.66 mmol) and 60 mL of
THF. The solution was cooled to 0° C with rapid stirring, followed by addition of isopropyl magnesium chloride (14.45 mL, 20.66 mmol) dropwise. The reaction was stirred for 1 h at 0° C. To a separate nitrogen-purged 250 mL 3-neck flask was added dry ice. The sublimed CO₂ was transferred via cannula and bubbled into the reaction for 1 h, followed by additional stirring for one hour. A white precipitate was observed. The solvent was removed under vacuum and the resulting salt was dissolved in water and washed with hexanes. The product was precipitated by acidification with 6M HCl and filtered to yield 2.5 g 2-bromo-5-thiophenoic acid (58%). ¹H NMR (CDCl₃, 300 MHz) δ (ppm): 7.63 (d, 1H, J=3.9 Hz), 7.11 (d, 1H, J=3.9 Hz). To a nitrogen-purged 100 mL 3-neck flask fitted with a distillation apparatus was added 2-bromo-5-thiophenoic acid (2.5 g, 12.07 mmol) and SOCl₂ (17.22 g, 144.7 mmol). The reaction was stirred overnight. The following morning, the temperature was increased to 80° C for 1 h, and distilled under vacuum to yield pure 5-bromothiophene-2-acetyl chloride as a yellow solid (assumed quantitative yield). This was dissolved in 10 mL dry DCM and added dropwise to a separate nitrogen-purged 3-neck flask cooled to 0° C containing ferrocene (3.34 g, 17.95 mmol) and AlCl₃ (1.61 g, 12.07 mmol) in 100 mL dry DCM with rapid stirring. After 3 h stirring, TLC indicated complete conversion. The reaction was neutralized slowly with nanowater, poured into ice water, and extracted with DCM. The extract was dried over MgSO₄, filtered, concentrated, and flashed through a column of silica gel using 2:8 hexane:EtOAc as the eluent to yield 1.84 g pure ferrocen-2-yl(5-bromothiophen-2-yl)methanone (41%). ¹H NMR (CDCl₃, 300 MHz) δ (ppm): 7.660 (d, 1H, J=4 Hz), 7.115 (d, 1H, J=4 Hz), 4.982 (t, 2H, J=1.8 Hz), 4.606 (t, 2H, J=1.8 Hz), 4.225 (s, 5H). To
a 250 mL nitrogen-purged 3-neck flask fitted with a reflux condenser containing 40 mL dry THF was added ferrocen-2-yl(5-bromothiophen-2-yl)methanone (1.50 g, 4.003 mmol), AlCl₃ (.907 g, 6.80 mmol), and finely powdered NaBH₄ (.605 g, 16.01 mmol). The resulting solution was vigorously refluxed for 2 h, upon which the solution color changed to orange. The reaction was allowed to cool to room temperature and slowly neutralized with nanowater, poured over ice water, extracted with DCM, dried over MgSO₄, filtered, and concentrated. The resulting concentrated solution was flashed through a column of silica gel using hexanes as the eluent to yield 1.3 g of 2-ferrocenyl-5-bromothiophene as a crystalline orange solid (86%). ¹H NMR (CDCl₃, 300 MHz) δ (ppm): 6.758 (d, 1H, J=3.7 Hz), 6.451 (d, 1H, J=3.7 Hz), 4.063 (s, 5H), 4.041 (s, 2H), 3.734 (s, 2H). ¹³C NMR (CDCl₃, 300 MHz) δ (ppm): 146.54, 129.67, 125.00, 109.58, 86.89, 68.91 (5C), 68.53 (2C), 67.97 (2C), 30.82.

**Figure 3.2.** Synthetic route to 8-(5-bromothiophene-2-yl)octane-1-thiol. a) nBuLi, 1,8-dibromooctane. b) NBS, DMF. c) thiourea, NaOH, HCl

**8-(5-bromothiophene-2-yl)octane-1-thiol (Figure 3.2).** To a nitrogen-purged 3-neck pear flask was added thiophene (1.5 g, 17.82 mmol) and 30 mL of THF. The solution was cooled to -78 °C and nBuLi (11.13 mL, 17.82 mmol) was added dropwise. The reaction was allowed to stir at -78 °C for 1 h. This was transferred dropwise via cannula to separate nitrogen-purged 3-neck flask
containing dibromooctane (10 g, 36 mmol) and 40 mL of THF at -78 °C. The reaction was allowed to warm to room temperature overnight. The reaction was poured into ice water, extracted with hexanes, dried over MgSO₄, filtered, and concentrated. The excess dibromooctane was removed via distillation in the first fraction, and 1.84 g of 2-(8-bromooctyl)thiophene was obtained in the second fraction as a clear oil (38%). ¹H NMR (CDCl₃, 300 MHz) δ (ppm): 7.102 (d, 1H, J=5.4 Hz), 6.912 (t, 1H, J=3.9 Hz) 6.772 (d, 1H, J=3.2 Hz), 3.401 (t, 2H, J=6.4 Hz), 2.817 (t, 2H, J=7.9 Hz), 1.849 (p, 2H, J=7.8 Hz), 1.673 (p, 2H, J=6.8 Hz), 1.391 (m, 8H). To a 100 mL 3-neck flask was added 2-(8-bromooctyl)thiophene (1.84 g, 6.67 mmol) and 20 mL of DMF. In one portion was added NBS (1.3 g, 7.3 mmol) and the reaction was allowed to stir at room temperature overnight. The reaction was poured into ice water, extracted with hexane, dried over MgSO₄, filtered, and concentrated. The concentrate was flashed through a column of silica gel using hexanes as the eluent to yield 2.18 g 5-bromo-2-(8-bromooctyl)thiophene (92%). ¹H NMR (CDCl₃, 300 MHz) δ (ppm): 6.835 (d, 1H, J=3.5 Hz), 6.524 (d, 1H, J=3.6 Hz), 3.40 (t, 2H, J=6.9 Hz), 2.732 (t, 2H, J=7.6 Hz), 1.847 (p, 2H, J=7.1 Hz), 1.623 (p, 2H, J=7 Hz), 1.397 (m, 8H). The well-known thiourea route was used for the next step. To an argon purged 250 mL 3-neck flask fitted with a reflux condenser was added 5-bromo-2-(8-bromooctyl)thiophene (2.18 g, 6.15 mmol), thiourea (1.17 g, 15.37 mmol) and 100 mL of degassed ethanol. The reaction was refluxed overnight. The reaction was cooled to room temperature and 30 mL of 1M NaOH was added. The reaction was refluxed for an additional 4 h, cooled to room temperature, and brought to neutral pH with dilute HCl. The solvent was removed, diluted with DCM, washed with brine
3x, dried over MgSO₄, filtered, and concentrated. The concentrate was flashed through a column of silica gel using 1:10 EtOAc:Hex as the eluent to yield 1.5 g 8-(5-bromo thiophene-2-yl)octane-1-thiol (79%). ¹H NMR (CDCl₃, 300 MHz) δ (ppm): 6.838 (d, 1H, J=3.7 Hz), 6.526 (d, 1H, J=3.7 Hz), 2.740 (t, 2H, J=7.6 Hz), 2.519 (q, 2H J=7.2 Hz), 1.625 (p, 4H, J=7.3 Hz), 1.2-1.5 (m, 9H). ¹³C NMR (CDCl₃, 300 MHz) δ (ppm): 129.61, 124.63, 34.04, 31.81, 31.48, 30.44, 28.57, 28.18, 24.77, 22.86.

Figure 3.3. Synthetic route to 8-(5-bromo-3-methyl-thiophene-2-yl)octane-1-thiol. a) LDA, -78 °C, 1,8-dibromooctane. b) thiourea, NaOH, HCl

8-(5-bromo-3-methyl-thiophene-2-yl)octane-1-thiol (Figure 3.3). LDA was made in situ via addition of nBuLi (40 mmol, 25 mL) to diisopropylamine (44 mmol, 4.45 g) in 40 mL THF at -78 °C. To a solution of 2-bromo-3-methylthiophene (7.08g, 40 mmol) in 40 mL THF at -78 °C was added the LDA solution dropwise. After stirring for 1 h, the resulting solution was transferred to a 250 mL 3-neck flask containing 1,8-dibromooctane (27.2 g,100 mmol) in 80 mL THF at -78 °C. This was allowed to warm to room temperature overnight. The solvent and 1,8-dibromooctane was removed under vacuum. After column chromatography using hexanes as the eluent yielded 9.6 g 2-bromo-5-(8-bromooctyl)-3-methylthiophene (65 %) ¹H NMR (CDCl₃, 300 MHz) δ (ppm): 6.457 (s, 1H), 3.403 (t, 2H, J=6.8 Hz), 2.682 (t, 2H, J= 7.3 Hz), 2.116 (s, 3H), 1.851 (p, 2H, J=7.5 Hz), 1.606 (m, 2H, J=7.3 Hz), 1.424 (p, 2H, J=7.3 Hz), 1.317 (m, 6H). ¹³C NMR (CDCl₃, 300 MHz) δ (ppm):
145.43, 136.81, 126.54, 105.76, 34.18, 32.98, 31.50, 30.45, 29.32, 29.04, 28.83, 28.32, 15.37. The well-known thiourea route was used for the next step. To an argon purged 250 mL 3-neck flask fitted with a reflux condenser was added g 2-bromo-5-(8-bromooctyl)-3-methylthiophene (3.68 g, 10 mmol), thiourea (1.9 g, 25 mmol) and 100 mL of degassed ethanol. The reaction was refluxed overnight. The reaction was cooled to room temperature and 40 mL of 1M NaOH was added. The reaction was refluxed for an additional 4 h, cooled to room temperature, and brought to neutral pH with dilute HCl. The solvent was removed, diluted with DCM, washed with brine 3x, dried over MgSO₄, filtered, and concentrated. The concentrate was flashed through a column of silica gel using 1:10 EtOAc:Hex as the eluent to yield .5 g 8-(5-bromo-3-methyl-thiophene-2-yl)octane-1-thiol (15 %).¹H NMR (CDCl₃, 300 MHz) δ (ppm): 6.453 (s, 1H), 2.676 (t, 2H, J=8.1 Hz), 2.515 (q, 2H, J=7.3 Hz), 2.112 (s, 3H), 1.601 (p, 4H, J=7.6 Hz), 1.306 (m, 8H).¹³C NMR (CDCl₃, 300 MHz) δ (ppm): 145.40, 136.90, 126.38, 105.80, 34.16, 31.43, 30.49, 29.39, 29.31, 28.52, 24.84, 22.69, 15.33.

**Figure 3.4.** Synthetic route to 2-bromo-3-methyl-5-iodothiophene. a) NBS, THF, 0 °C. b) iodine, iodobenzene diacetate, CHCl₃

**2-bromo-3-methyl-5-iodothiophene (Figure 3.4).** To a 3-neck flask was added 3-methylthiophene (9.818g, 100 mmol) and 100 mL THF. This was cooled to 0° C and NBS (17.798 g, 100 mmol) was added in one portion. This reaction was
allowed to warm to room temperature overnight. The solvent was removed, redissolved in ether, washed with water, dried over MgSO₄, and concentrated. The concentrated product was purified through an alumina plug using hexanes as the eluent to yield 13.2 g pure 2-bromo-3-methylthiophene as a colorless oil (75%). ¹H NMR (CDCl₃, 300 MHz) δ (ppm): 7.160 (d, 1H, J=5.4 Hz), 6.773 (d, 1H, J=5.8 Hz), 2.194 (s, 3H). To a solution of 2-bromo-3-methylthiophene (6.6 g, 37 mmol) in chloroform (60 mL) was added iodine (5.96 g, 18.5 mmol), followed by iodobenzene diacetate (4.695 g, 18.5 mmol). This was stirred at room temperature overnight. The following day, the reaction was washed with a dilute solution of sodium sulfite and water, dried over MgSO₄, and concentrated. The iodobenzene was distilled off under vacuum in the first fraction and 7.75 g pure 2-bromo-3-methyl-5-iodothiophene was obtained in the second fraction (70%). Flashing through an alumina plug can be beneficial. ¹H NMR (CDCl₃, 300 MHz) δ (ppm): 6.952 (s, 1H), 2.159 (s, 3H).

**Figure 3.5.** Synthetic route to 6-(5-bromothiophen-2-yl)hexyl)phosphonic acid. a) triethyl phosphite, 170 °C. b) BrSiMe₃, methanol

**6-(5-bromothiophen-2-yl)hexyl)phosphonic acid (Figure 3.5).** 2-(8-bromohexyl)thiophene was synthesized as reported previously.²⁰ Triethylphosphite (10.19 g, 61 mmol) and 2-(8-bromohexyl)thiophene (2 g, 6.1 mmol) was added to a 3-neck flask fitted with a reflux condenser. This solution was refluxed vigorously for 24 h. Upon cooling, excess triethylphosphite was removed under vacuum to yield
pure diethyl (6-(5-bromothiophen-2-yl)hexyl)phosphonate (assumed quantitative yield). $^1$H NMR (CDCl$_3$, 300 MHz) $\delta$ (ppm): 6.824 (d, 1H, $J$=4.1 Hz), 6.508 (d, 1H, $J$=4.1 Hz), 4.069 (m, 4H, $J$ = 3.5 Hz), 2.720 (t, 2H, $J$=7.6 Hz), 1.616 (m, 6H), 1.369 (m, 2H), 1.307 (t, 6H, $J$=7.3 Hz). $^{13}$C NMR (CDCl$_3$, 300 MHz) $\delta$ (ppm): 147.67, 129.65, 124.66, 108.97, 61.65, 31.34 (2C), 30.42 (2C), 28.50, 26.78, 24.84, 22.37, 16.81. In a 3-neck 100 mL flask was added diethyl (6-(5-bromothiophen-2-yl)hexyl)phosphonate and bromotrimethylsilane (1.87 mL, 14.1 mmol). This was allowed to stir overnight. The following day, excess trimethylsilane was removed under vacuum. Under nitrogen, methanol (30 mL) was added and this was brought to reflux for 4 h. The methanol was removed under vacuum to yield (6-(5-bromothiophen-2-yl)hexyl)phosphonic acid (quantitative yield). $^1$H NMR (CDCl$_3$, 300 MHz) $\delta$ (ppm): 6.822 (d, 1H, $J$=4.2 Hz), 6.511 (d, 1H, $J$=4.2 Hz), 2.718 (t, 2H, $J$=7.4 Hz), 1.614 (m, 5H), 1.368 (m, 5H). $^{13}$C NMR (DMSO-d$_6$, 300 MHz) $\delta$ (ppm): 148.09, 130.77, 126.00, 108.42, 49.09, 31.18, 29.97, 28.50, 26.99, 23.11.

![Figure 3.6. Synthetic route to (3-(5-bromo-4-methylthiophen-2-yl)propyl)trichlorosilane. a) isopropyl magnesium chloride, allyl bromide. B) HSiCl$_3$, H$_2$PtCl$_6$.](image)

(3-(5-bromo-4-methylthiophen-2-yl)propyl)trichlorosilane (Figure 3.6). To a 3-neck flask containing 2-bromo-3-methyl-5-iodothiophene (1.455 g, 4.80 mmol) in 20 mL THF was added isopropyl magnesium chloride (2.47 mL, 4.80 mmol) at 0 °C. This was stirred for 1 h and quenched with allyl bromide (0.7 g, 5.76
mmol). The THF was removed under vacuum and the product was redissolved in ether, washed with water and brine, dried over MgSO₄, and concentrated. The crude product was flushed through a plug of alumina to yield 1 g pure 2-bromo-3-methyl-5-allylthiophene (95.8%). ¹H NMR (CDCl₃, 300 MHz) δ (ppm): 6.499 (s, 1H), 5.918 (m, 1H), 5.121 (m, 2H), 3.439 (d, 2H, J=6.9 Hz), 2.121 (s, 3H). In a 3-neck flask was added 2-bromo-3-methyl-5-allylthiophene (1 g, 4.6 mmol), trichlorosilane, and one crystal of chloroplatinic acid hexahydrate. This was stirred at room temperature overnight. The following day, trichlorosilane as removed under vacuum to yield pure (3-(5-bromo-4-methylthiophen-2yl)propyl)trichlorosilane (quantitative yield). ¹H NMR (CDCl₃, 300 MHz) δ (ppm): 6.502 (s, 1H), 2.814 (t, 2H, J=7.2 Hz), 2.129 (s, 3H), 1.904 (p, 2H, J=8.4 Hz), 1.437 (t, 2H, J=8.4 Hz). ¹³C NMR (CDCl₃, 300 MHz) δ (ppm): 143.00, 137.04, 127.45, 106.53, 32.23, 24.30, 23.46, 15.72.

**Figure 3.7.** Synthetic route to (4-bromobenzyl)phosphonic acid. a) triethyl phosphite, 170 °C. b) BrSiMe₃, methanol

**(4-bromobenzyl)phosphonic acid (Figure 3.7).** In a 3-neck 100 mL flask was added triethylphosphite and 4-bromobenzyl bromide. This was heated to reflux for 24 h. Upon cooling, excess triethylphosphite was removed under vacuum to yield pure diethyl 4-bromobenzylphosphonate (quantitative yield). ¹H NMR (CDCl₃, 300 MHz) δ (ppm): 7.435 (d, 2H, J=8.6 Hz), 7.174 (dd, 2H, J=8.6 Hz), 4.023 (p, 4H, J=7.2
Hz), 3.140 (d, 2H, J=21.5 Hz), 1.251 (t, 6H, J=7.1 Hz). To a 3-neck flask was added diethyl 4-bromobenzylphosphonate (1.22 g, 4 mmol) and bromotrimethylsilane (2 g, 13 mmol). This was stirred overnight. Excess trimethylsilane was removed under vacuum and methanol (30 mL) was added under nitrogen. This was refluxed for 4 h. The methanol was removed under vacuum to yield pure (4-bromobenzyl)phosphonic acid (quantitative yield). $^1$H NMR (CDCl$_3$, 300 MHz) δ (ppm): 7.447 (d, 2H, J=8.5 Hz), 7.181 (dd, 2H, J=8.5 Hz), 2.921 (d, 2H, J=21.3 Hz).

**Figure 3.8.** Synthetic route to (11-oxo-11-ferrocenylundecyl)phosphonic acid. a) thionyl chloride. b) ferrocene, AlCl$_3$, 0 °C. c) triethyl phosphite, reflux. d) bromotrimethylsilane, methanol

(11-oxo-11-ferrocenylundecyl)phosphonic acid (Figure 3.8). To a 3-neck flask containing 11-bromoundecanoic acid (5.3 g, 20 mmol) and DCM (10 mL) was added thionyl chloride (2.9 mL, 40 mmol). This was stirred at room temperature overnight. The following day, DCM and excess thionyl chloride was removed under vacuum, and the product was distilled under vacuum and added dropwise to a 3-
neck flask containing ferrocene (7.44 g, 40 mmol) and AlCl$_3$ (4 g, 30 mmol) in 60 mL DCM at 0 °C. This was stirred at room temperature overnight. The solution was neutralized with nanowater, poured over water, and extracted with DCM. The product was concentrated and purified on a silica gel column using 1:9 EtOAc:hexanes as the eluent to yield 5.68 g 11-bromoundecanoylferrocene (57 %).$^1$H NMR (CDCl$_3$, 300 MHz) δ (ppm): 4.779 (t, 2H, J=1.7 Hz), 4.487 (t, 2H, J=1.7 Hz), 4.193 (s, 5H), 3.407 (t, 2H, J=6.5 Hz), 2.692 (t, 2H, J=7.6 Hz), 1.854 (p, 2H, J=6.9 Hz) 1.700 (p, 2H, J=7.2 Hz), 1.315 (m, 12H). To a 3-neck flask was added 11-bromoundecanoylferrocene (2.16 g, 5 mmol) and triethyl phosphite (8.3 g, 50 mmol). This was heated to reflux overnight. The following day, excess triethyl phosphite was distilled off to yield pure diethyl (11-oxo-11-ferrocenylundecyl)phosphonate (2.1 g).$^1$H NMR (CDCl$_3$, 300 MHz) δ (ppm): 4.780 (t, 2H, J=1.9 Hz), 4.485 (t, 2H, 1.9 Hz), 4.194 (s, 5H), 4.085 (m, 4H), 2.690 (t, 2H, J=7.3 Hz), 1.667 (m, 8H), 1.320 (t, 6H, J=6.5 Hz), 1.343 (m, 10H). To a 3-neck flask was added diethyl (11-oxo-11-ferrocenylundecyl)phosphonate (2.1 g, 4.3 mmol) and bromotrimethylsilane (1.98 g, 12.9 mmol). This was stirred at room temperature overnight. The following day, bromotrimethylsilane was removed and methanol (30 mL) was added. This was heated to reflux for four h. The methanol was removed under vacuum, and the product was redissolved in dilute base, precipitated by addition of 6 M HCl, filtered, and dried to yield .6 g (11-oxo-11-ferrocenylundecyl)phosphonic acid as a brown solid (33 %). The NMR J couplings could not be resolved due to limited solubility in CDCl$_3$. $^1$H NMR (CDCl$_3$, 300 MHz) δ (ppm): 4.766 (2H), 4.461 (2H), 4.165 (5H), 2.663 (2H), 1.621 (8H), 1.281 (10H).
**Preparation of Si-KCTP initiator substrates.** Silicon wafers (Silicon Quest) and glass slides (VWR) were cut into 2 × 3 cm rectangles and subjected to plasma cleaning using argon plasma (Harrick Plasma) for 5 min. The substrates were then treated for 15 min in a UV-ozone cleaner and transferred to a nitrogen-filled glove box. 40 µL of 3-(5-bromo-4-methylthiophene-2-yl)propyltrichlorosilane was dissolved in 10 mL of toluene, and the solution was poured over the substrates, which were capped and left overnight. The substrates were then removed from the solution, sonicated one minute in toluene, one minute in DCM, one minute in IPA, and finally rinsed with IPA. The substrates were dried in a stream of nitrogen gas and transferred back inside a glovebox. For gold substrates, the same cleaning procedure was used, but without the UV-ozone treatment. The cleaned substrates were then placed in a 5 mM toluene solution of 8-(5-bromothiophene-2-yl)octane-1-thiol overnight. Substrates were then removed from the solution, rinsed as described above, and transferred back inside a glove box. For ITO, the substrates were sonicated in 18 MΩ and isopropanol for 15 minutes followed by cleaning using a H₂O₂:NH₄OH:H₂O bath (1:1:5) at 80 °C for 1 h. Slides were extensively rinsed with water and ethanol, and placed in a 5mM ethanol solution of the phosphonic acid self-assembly molecule for 48 h. Contact angle after cleaning was <10° and after self-assembly 75°.

**Magnesiation of 2-ferrocenyl-5-bromothiophene.** To a 40 mL THF solution of 2-ferrocenyl-5-bromothiophene (0.288 g, .797 mmol) at 0 °C was added isopropyl magnesium chloride (0.36 mL, 0.7173 mmol). This was allowed to stir for 30 minutes at 0 °C and then 1 h at room temperature. This solution was then
transferred to the glovebox. NMR confirmed complete conversion upon quenching with D$_2$O.

**Magnesiation of 2-bromo-5-iodo-3-methylthiophene.** To a 20 mL THF solution of 2-bromo-5-iodo-3-methylthiophene (0.302 g, 1 mmol) was added isopropyl magnesium chloride (0.45 mL, 0.9 mmol). This was allowed to stir for 1 h at 0 °C and then 30 min at room temperature. This solution was then transferred to the glovebox.

**Formation of Initiators.** In a glovebox, 30 mg of Ni(COD)$_2$ and 17 mg of 2,2-bipyridine (bpy), 43 mg dppe, 45 mg dppp, or 46 mg of dppb was weighed out in a 20 mL scintillation vial, followed by the addition of 10 mL toluene. Silicon, gold or ITO substrates containing an aryl bromide monolayer was placed in the solution. For the ligand exchange step from bpy, the substrates were extensively rinsed with toluene and placed in a 10 mL 0.1M toluene solution of dppe, dppp, or dppb for 1 h. Just prior to polymerization, substrates were removed from the ligand exchange solution and rinsed extensively with toluene and THF.

**Ellipsometric measurements.** Null ellipsometry measurements of monolayers were performed on a Multiskop (Optrel GbR) with a 632.8 nm HeNe laser light source at 70°. Film thickness was obtained by fitting ellipsometric data using manufacturer provided specialized software. At least three spots on each wafer were measured, and the thickness was averaged. To obtain thickness values of the samples, a simple box model was employed and a refractive index of $n = 1.5$, $k = 0$ was used.
**Electrochemical measurements.** Electrochemical measurements were obtained using a CH Instruments bipentiostat equipped with a platinum counter electrode and a silver wire pseudo reference electrode. The gold substrates were used as the working electrode. Tetrabutylammonium hexafluorophosphate in DCM (.1M, degassed) was used as the supporting electrolyte. All scan rates are recorded at 100 mV/sec unless otherwise noted.

**FTIR measurements.** Infrared spectra of films were acquired using a Thermo-Nicolet Model 6700 spectrometer equipped with a variable angle grazing angle attenuated total reflection (GATR-ATR) accessory (vari-GATR, Harrick Scientific) and processed using OMNIC 8.0 software (ThermoNicolet, Madison, WI).

**UV-VIS measurements.** UV-vis spectra of polymer substrates were taken using a Cary 50 UV-vis spectro-photometer from Varian. Variable angle polarized light UV-Vis was performed using a custom-built variable angle sample holder fitted with a rotatable polarizing filter.

**Discussion and Results**

**Fabrication of SI-KTCP initiators.** Immobilization of external initiators onto planar and spherical substrates is an effective strategy toward SI-KTCP.\textsuperscript{19, 23} The fabrication of such initiators is accomplished through oxidative addition of Ni(0) complexes to a surface-bound aryl halogen bond, which generates an aryl-Ni(II)-halogen species. Early attempts to use Ni(PPh\textsubscript{3})\textsubscript{4} as a source of Ni(0) yielded poor results. It has been speculated that coordinately saturated Ni(PPh\textsubscript{3})\textsubscript{4} is not reactive enough for interfacial chemistry.\textsuperscript{20, 25} Furthermore, attempts to immobilize
Ni(0) onto organosilica particles using Ni(PPh₃)₄ resulted in unsuccessful polymerizations.²⁶ Utilization of Ni(COD)₂ as the source of Ni(0) combined with triphenylphosphine (PPh₃) has led to successful results, where the weakly dissociating COD ligands are displaced by PPh₃.²⁰ The success of this result was due to the formation of a reactive intermediate Ni(COD)(PPh₃)₂ species. Unfortunately, PPh₃ as an attendant ligand is notorious for poor results in KCTP relative to bidentate dppp and dppe. The direct incorporation of dppp or dppe into SI-KCTP initiators is not a trivial task, since Ni(dppp)₂ and Ni(dppe)₂ complexes are nearly inert toward oxidative addition.²⁷ In this report, Ni(COD)₂ is used in conjunction with a variety of σ-donating ligands to fabricate initiators for SI-KCTP.

![Molecules used for self-assembly](image)

**Figure 3.9.** Molecules used for self-assembly.

Aryl-halide molecules for self-assembly on Au and ITO substrates were synthesized (Figure 3.9). For self-assembled monolayers (SAMs) on gold (molecules
1 and 2), an eight-carbon aliphatic chain allows the formation of a well-packed monolayer due to thermodynamically favorable van der Waals interactions, even in the presence of bulky aryl groups.\textsuperscript{28} Polarization-modulation infrared reflection-absorption spectroscopy (PM-IRRAS) was used to demonstrate aliphatic stretching frequencies characteristic of a crystalline-like interface (Figure 3.10).\textsuperscript{29}

![Figure 3.10](image.png)

**Figure 3.10.** Baseline corrected PM-IRRAS image of 1 (red line) and 2 (black line) on gold.

Cyclic voltammetry (CV) was used to verify the absence of pinhole defects in the monolayer.\textsuperscript{30} Additionally, monolayer coverage values of \(6 \times 10^{14}\) molecules/cm\(^2\) and \(4.5 \times 10^{14}\) molecules/cm\(^2\) were obtained through integration of the oxidation wave in the cyclic voltammogram for 1 and 2, respectively.\textsuperscript{31} Monolayers of 2 yield slightly lower coverage, presumably due to the bulky methyl group. Phosphonic acid derivatives 3-5 are used to fabricate stable monolayers on ITO.\textsuperscript{32} Phosphonic acids as anchoring groups are advantageous over chlorosilane...
analogs due in part to the lack of HCl byproducts that can etch the ITO layer, while also offering selectivity for ITO over other substrate types. It is known that ITO has a limited surface hydroxyl content relative to silicon, and the packing density of monolayers formed is lower than gold.\textsuperscript{33} The maximum monolayer packing density of ITO surfaces was directly measured by CV through the self-assembly of ferrocenyl functionalized phosphonic acid 5. Integration of the anodic and cathodic waves yields an average packing density of 2×10^{14} molecules/cm\textsuperscript{2} for ITO surfaces, similar to previous reports.\textsuperscript{34} The packing density is approximately three times lower than 1 and 2 on gold. Silane derivative 6 is used for self-assembly on Si/SiO\textsubscript{2} wafers. The catalyst/ligand combinations used to fabricate immobilized (aryl)Ni(II)-Br complexes were Ni(COD)\textsubscript{2} mixed with 1 equiv. of dppe, dppp, or 2-2' -bipyridine (bpy). Each catalyst/ligand combination resulted in a different Ni(0) complex yielding a uniquely colored solution: bright yellow for Ni(COD)\textsubscript{2} + dppe, yellow-orange for Ni(COD)\textsubscript{2} + dppp, and violet for Ni(COD)\textsubscript{2} + bpy. Substrates incorporating an aryl bromide monolayer were exposed to the different catalyst/ligand combinations for 20 hours to generate surface-bound (aryl)Ni(II)-Br as shown in Figure 3.11. Although the reaction was allowed to proceed 20 hours to ensure completion, no significant difference in (aryl)Ni(II)-Br coverage was observed with a one hour time frame. Extensive rinsing was used to remove any physisorbed Ni(0) complexes prior to Kumada reactions.
Figure 3.11. Fabrication of SI-KCTP initiators on gold via 1 using Ni(COD)$_2$ + bpy, 2 equiv. PPh$_3$, dppe, or dppp.

**Quantitative characterization of immobilized Ni(II) complexes.**

Experimental constraints restrict the direct measurement of (aryl)Ni(II)-Br with cyclic voltammetry and PM-IRRAS, presumably due to the instability of the species in electrolytic medium and weak phosphorous/aromatic C-H stretching frequencies. Therefore, to quantify the resulting surface-bound initiators, an indirect electrochemical probe was employed. Ferrocene demonstrates a stable and reversible redox couple, which can be utilized through a ferrocene derivative that is capable of undergoing magnesium-halogen exchange to generate a “capping” agent (7 in Figure 3.11). By reacting 7 with nickel (II) initiators immobilized on a conducting substrate, a surface-bound redox couple is generated, as shown in Figure 3.11. Utilizing CV, the surface coverage of tethered ferrocene and thus, the percent yield of the coupling reaction can be obtained by integration of the oxidation or reduction wave. This is based on the valid assumption that quantitative conversion
of the nickel (II) initiators occurs. Also, due to the sensitivity of cyclic voltammetry with respect to the structure and dynamics of SAMs, this technique not only allows for quantification of initiator densities, but also provides information about the spatial proximity of initiators, and SAM integrity.\textsuperscript{35}

Figure 3.12. a) A cyclic voltammogram of bpy-based initiators using SAMs of 1 after reaction with the ferrocene capping agent. Arrow indicates scan direction. b) Plot of I(peak)/I(background) vs. log (frequency) prepared using ac voltammetry. The red circles represent the data and and the black squares represent the fit to the data to obtain a rate constant of 55 s\textsuperscript{-1}. The red and black lines are to guide the eye.

Table 3.1. Surface densities of (aryl)Ni(II)-Br complexes obtained from the reaction of SAMs generated from 1 on gold with Ni(COD)\textsubscript{2} + ligand after 20 hours.

<table>
<thead>
<tr>
<th>Ligand</th>
<th>Coverage molecules/cm\textsuperscript{2}\textsuperscript{a} (x10\textsuperscript{13})</th>
<th>Yield (%)\textsuperscript{b}</th>
<th>FWHM (mV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2 equiv. PPh\textsubscript{3}</td>
<td>6.00</td>
<td>10</td>
<td>120</td>
</tr>
<tr>
<td>dppe</td>
<td>4.84</td>
<td>8.1</td>
<td>116</td>
</tr>
<tr>
<td>dppp</td>
<td>4.14</td>
<td>6.9</td>
<td>122</td>
</tr>
<tr>
<td>bpy</td>
<td>5.16</td>
<td>8.6</td>
<td>95</td>
</tr>
</tbody>
</table>

\textsuperscript{a}Calculated as the average of at least two trials.

\textsuperscript{b}Yield (%) calculated by dividing ferrocene surface coverage in column 2 by original SAM coverage of 1 (6.00x10\textsuperscript{14} molecules/cm\textsuperscript{2}).
After 4 hours, the Kumada coupling reaction of (aryl)Ni(II)-Br with organomagnesium capping agent 7 (0.02 M) is complete. CV experiments revealed clear anodic and cathodic waves in which the current scales linearly with scan rate, indicating a surface-bound redox couple. Figure 3.12, which shows results of the bpy-based complex, is representative of all studied Ni/ligand combinations (CVs of reactions involving 2PPh₃-, dppe- and dppp-based complexes are shown in Figures 3.13-3.15).

**Figure 3.13.** CV of 2PPh₃-based initiators after capping agent reaction using SAM of 1. Arrow indicates start of the scan.
**Figure 3.14.** CV of dppe-based initiators after capping agent reaction using SAM of 1. Arrow indicates start of the scan.

**Figure 3.15.** CV of dppp-based initiators after capping agent reaction using SAMs of 1. Arrow indicates start of the scan.
The low capacitive charging current in Figure 3.12 is representative of a pinhole free interface. Table 3.1 provides a summary of surface coverage values obtained for all ligand combinations. The full width at half maximum (FWHM) gives insight into the spatial homogeneity of redox sites on the surface, where a value of 90.6 mV is characteristic of a Nernstian, one-electron redox couple. Broad redox peaks indicate kinetic heterogeneity. When 2PPh₃, dppe, and dppp were used as ligands with Ni(COD)₂ (Figures 3.13, 3.14, and 3.15, respectively), the FWHM was ~120 mV, suggesting the presence of a number of different initiator environments. When using bpy, a FWHM of 91-100 mV is obtained (Figure 3.12), which is near the ideal Nernstian value, implying that initiators are evenly distributed across the substrate with a calculated surface coverage of 8.6 %. The estimated rate of electron transfer is 55 s⁻¹ using an alternating current (AC) voltammetry technique developed by Creager et al. (Figure 3.12). This rate of electron transfer is comparable to other rates calculated in systems of similar tether links, which indicates a homogenous, defect-free monolayer even after harsh cross-coupling conditions. The surface coverage of Ni(II) obtained using Ni(COD)₂/bpy was also relatively high (5.2x10¹³ molecules/cm²). In summary, the use of Ni(COD)₂/bpy as the catalyst system yields a high coverage and a homogenous distribution of immobilized Ni(II) species. For these reasons, Ni(COD)₂/bpy was chosen as the catalyst system for further experiments.
Figure 3.16. Ligand exchange from bpy-based initiator to dppe-, dppp-, or dppb-based initiators using SAMs of 1 and 2 on gold.

**Initiator Ligand exchange.** With respect to SI-KCTP, the use of bpy as a ligand results in predominantly step-growth character.\(^{26}\) Therefore, ligand exchange reactions are commonly employed to create chain-growth character in solution- and surface-based KCTP.\(^{26, 40}\) Generation of CPs with controlled molecular weight and low polydispersity require bidentate phosphine ligands. Bronstein et al. first reported a ligand exchange procedure to generate external initiators that incorporate bidentate dppp for KCTP.\(^{40}\) In their approach, Ni(PPh\(_3\))\(_4\) was reacted with chlorobenzene to generate (Ph)Ni(PPh\(_3\))\(_2\)-Cl, followed by ligand exchange with dppp to generate (Ph)Ni(dppp)-Cl. This entropically driven reaction has resulted in external initiators that provide excellent KCTP performance with respect to controlled molecular weight and low polydispersity. Senkovskyy et al. shortly
thereafter provided an alternative method of fabricating bidentate phosphine external initiators, where diethyl bipyridal Ni(0) (Et₂Ni(bpy)) is exposed to aryl bromides to generate (Ph)Ni(bpy)-Br.²⁶ In the presence of dppp, a stronger σ-donor, ligand exchange occurs to generate (Ph)Ni(dppp)-Br. It was also noted that extensive homocoupling reactions take place when using Ni(PPh₃)₄ to generate external initiators, while the use of Et₂Ni(bpy) proceeds cleanly.⁴¹,⁴²

**Table 3.2.** SI-KCTP initiator coverage values obtained after ligand exchange from bpy-based initiators using SAMs of 1 on gold.

<table>
<thead>
<tr>
<th>Ligand</th>
<th>Coverage molecules/cm²</th>
<th>Yield (%)</th>
<th>Overall Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>bpy</td>
<td>5.16 ×10¹³</td>
<td>N/A</td>
<td>8.6</td>
</tr>
<tr>
<td>dppe</td>
<td>2.81</td>
<td>54</td>
<td>4.7</td>
</tr>
<tr>
<td>dppp</td>
<td>2.19</td>
<td>42</td>
<td>3.7</td>
</tr>
<tr>
<td>dppb</td>
<td>4.68</td>
<td>90</td>
<td>7.8</td>
</tr>
</tbody>
</table>

*Calculated as the average of at least two trials.

*bYield (%) calculated from dividing coverage after ligand exchange by coverage before ligand exchange (5.16×10¹³).

*cOverall Yield (%) calculated from dividing coverage by monolayer coverage of 1 (6.00×10¹⁴).

Surface-bound Ni(II) initiators ligated by dppe or dppp are generated according to Figure 3.16. This is accomplished by immersion of the substrate in a 0.025 M toluene solution of bidentate ligand for one hour. The substrates are then extensively rinsed with THF and placed in a 0.02 M solution of organomagnesium complex 7. Table 3.2 lists the surface coverage values of (aryl)Ni(II)-Br with bidentate phosphines obtained from 1 after ligand exchange from the bpy-based Ni(II) complex. According to the data, the ligand exchange reaction resulted in a substantial loss in SI-KCTP initiator coverage, with dppp exhibiting the greatest loss
(58%). This is attributed to interfacial homocoupling reactions (disproportionation), as shown in Figure 3.17. Yamamoto proposed the formation of a dinuclear Ni-complex with aryl and bromo ligands as the intermediate in the disproportion reaction,\(^{43}\) and the close proximity of Ni on the surface may facilitate this reaction.\(^{22,24}\) Other groups have observed disproportionation with KCTP, where two polymer chains couple together when quenching the polymerization with methanol or water.\(^{44,45}\) Yokozawa \textit{et al.} argued that this methanol quenching effect was a result of a change in the ligand environment of the nickel catalyst.\(^{44}\) Doubina \textit{et al.} described a degradation of a thiophene-based initiator structure after ligand exchange from PPh\(_3\) to dppp, which most likely resulted from a disproportionation reaction.\(^{46}\) To determine if this trend is observed with larger bite angles, dppb (bite angle of 98°) was also investigated (Table 3.3). No loss in initiator coverage was observed, which we speculate is caused by trans-complex geometry, rather than cis, around the nickel center, as observed earlier by other groups in palladium complexes.\(^{47,48}\) Another difference with dppb relative to dppe and dppp is reduced solubility in toluene. To eliminate this as a contributing factor due to any concentration differences in the experimental results, ligand exchange reactions were performed at low concentrations (2.5 mM) of dppe, dppp, and dppb (Table 3.4). These experiments yielded similar results as was expected, due to the large excess of ligand in solution relative to Ni(II) on the surface.
Figure 3.17. Proposed mechanism of the reduction in surface density of Ni(II) through disproportionation on gold.

Table 3.3. Initiator coverages using low concentration of exchange ligand (2.5 mM) using SAMs of 1. Catalyst deposition time was one hour.

<table>
<thead>
<tr>
<th>Ligand</th>
<th>Coverage (molecules/cm²)</th>
<th>Yield (%)&lt;sup&gt;a&lt;/sup&gt;</th>
<th>Overall Yield (%)&lt;sup&gt;b&lt;/sup&gt;</th>
<th>Yield (%)&lt;sup&gt;c&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>bpy</td>
<td>3.00&lt;sup&gt;c&lt;/sup&gt;</td>
<td>N/A</td>
<td>5</td>
<td></td>
</tr>
<tr>
<td>dppe</td>
<td>2.17</td>
<td>72</td>
<td>3.6</td>
<td></td>
</tr>
<tr>
<td>dppe</td>
<td>1.81</td>
<td>60</td>
<td>3</td>
<td></td>
</tr>
<tr>
<td>dppp</td>
<td>0.713</td>
<td>24</td>
<td>1.1</td>
<td></td>
</tr>
<tr>
<td>dppp</td>
<td>0.913</td>
<td>30</td>
<td>1.5</td>
<td></td>
</tr>
<tr>
<td>dppb</td>
<td>2.02</td>
<td>67</td>
<td>3.3</td>
<td></td>
</tr>
<tr>
<td>dppb</td>
<td>2.04</td>
<td>68</td>
<td>3.4</td>
<td></td>
</tr>
</tbody>
</table>

<sup>a</sup>Yield (%) of ligand exchange was calculated by dividing initiator coverage by bpy-based initiator coverage (3.0×10<sup>13</sup> initiators/cm²).

<sup>b</sup>Overall Yield (%) was calculated by dividing initiator coverage by monolayer coverage for 1 (6×10<sup>14</sup> molecules/cm²).

<sup>c</sup>Ni(COD)bpy reaction time was one hour in this case.

Reports have demonstrated that aliphatic substituents ortho to the nickel complex can impede disproportionation reactions.<sup>46, 49, 50</sup> To investigate whether this is indeed an effective strategy to generate stable (aryl)Ni(II)-Br complexes, compound 2, with a methyl substituent ortho to the halogen was synthesized. Table 3.4 lists SI-KCTP initiator coverage before and after ligand exchange using 2. In general, the percent yield of the ligand exchange reaction was greatly improved.
from 42% to 65% for dppp and 54% to 85% with dppe; however, homocoupling reactions are still present, as demonstrated by the slight decrease in coverage among the bidentate ligands relative to the bpy complex. It is important to note that although these results agree with previous reports that substituents ortho to the nickel can impede disproportionation, the net overall coverage of (aryl)Ni(II)-Br is lower, due to the steric influence of the 3-methyl substituent on the monolayer packing density.

Table 3.4. SI-KCTP initiator coverage values after ligand exchange from bpy-based initiators using SAMs of 2 on gold.

<table>
<thead>
<tr>
<th>Ligand</th>
<th>Coverage molecules/cm²</th>
<th>Yield (%)</th>
<th>Overall Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>bpy</td>
<td>1.67 ×10¹³</td>
<td>N/A</td>
<td>3.7</td>
</tr>
<tr>
<td>dppe</td>
<td>1.43</td>
<td>85</td>
<td>3.1</td>
</tr>
<tr>
<td>dppp</td>
<td>1.08</td>
<td>65</td>
<td>2.4</td>
</tr>
</tbody>
</table>

*a* Calculated as the average of at least two trials.
*b* Yield (%) calculated by dividing surface coverage after ligand exchange by coverage before ligand exchange (1.67×10¹³ molecules/cm²)
*c* Overall Yield (%) calculated by dividing surface coverage by initial monolayer coverage of 2 (4.50×10¹⁴ molecules/cm²)

The reduced packing density of molecules in SAMs formed on ITO prompted an investigation into whether sterics play a role in facilitating disproportionation as was observed with SAMs on Au. Table 3.5 lists the coverage values of bpy-supported (aryl)Ni(II)-Br complexes, followed by coverage values of dppe, dppp, and dppb complexes after ligand exchange. No loss in Ni(II) coverage among any of the bidentate phosphines after ligand exchange was observed. In addition to the phenyl bromide based initiator 4 on ITO, thienyl bromide based initiator 3 was used to elucidate whether the nature of the aryl species contributed to the loss of coverage.
(Table 3.6). No difference between phenyl bromide and thienyl bromide species was observed, which implies that disproportionation due to the close proximity of initiators on gold was solely responsible for the loss in coverage after ligand exchange.

**Table 3.5.** SI-KCTP initiator coverage values after ligand exchange from bpy-based initiators using 4 on ITO.

<table>
<thead>
<tr>
<th>Ligand</th>
<th>Coverage (molecules/cm²)</th>
<th>Yield (%)</th>
<th>Overall Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>bpy</td>
<td>4.41d</td>
<td>N/A</td>
<td>22</td>
</tr>
<tr>
<td>dppe</td>
<td>4.46</td>
<td>~100</td>
<td>22</td>
</tr>
<tr>
<td>dppp</td>
<td>4.78</td>
<td>~100</td>
<td>24</td>
</tr>
<tr>
<td>dppb</td>
<td>3.80</td>
<td>86</td>
<td>19</td>
</tr>
</tbody>
</table>

*a*Calculated as the average of at least two trials.  
*b*Yield (%) calculated by dividing surface coverage after ligand exchange by coverage before ligand exchange (4.41×10¹³ molecules/cm²).  
*c*Overall Yield (%) calculated by dividing surface coverage by initial monolayer coverage of 4 (2.00×10¹⁴ molecules/cm²).  
*d*Ni(COD)(bpy) reaction time was one hour in this case.

**Table 3.6.** Initiator coverages using SAMs of 3.

<table>
<thead>
<tr>
<th>Ligand</th>
<th>Coverage (molecules/cm²)</th>
<th>Average Coverage (molecules/cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>bpy</td>
<td>1.50c</td>
<td>1.89c</td>
</tr>
<tr>
<td>bpy</td>
<td>2.28c</td>
<td></td>
</tr>
<tr>
<td>dppe</td>
<td>2.25</td>
<td>1.73</td>
</tr>
<tr>
<td>dppe</td>
<td>1.20</td>
<td></td>
</tr>
<tr>
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<td>dppb</td>
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<td>1.94</td>
</tr>
<tr>
<td>dppb</td>
<td>1.21</td>
<td></td>
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</tbody>
</table>

*e*Ni(COD)bpy reaction time was one hour in this case.
To gain insight into the surface-bound coupling reaction and also provide evidence that the ligand exchange reaction occurred, the rate constant of the cross-coupling with organomagnesium reagent 7 was determined among different initiator structures using SAMs of 1. Lanni et al. have previously demonstrated the sensitivity of the rate constant of KCTP to the ligand. For polymerizations involving dppe as the supporting ligand, reductive elimination was found to be rate limiting but with dppp, transmetallation was the rate limiting step. Incorporation of bidentate ligands with bulky substituents was found to have a large impact on the polymerization rate. In the present case with surface bound Ni(II) complexes, the pseudo-first order rate constant, \( k' \), can be obtained by monitoring the increase in ferrocene coverage, \( \Gamma_f \), with time, \( t \). Assuming effective mixing and a high concentration of organomagnesium complex in solution relative to (aryl)Ni(II)-Br on the surface, the model can be reduced to a pseudo-first order reaction, \( \ln \left[ \frac{\Gamma_f}{\Gamma_f - \Gamma_t} \right] = k't \)

where \( \Gamma_f \) is the final ferrocene coverage.

Figure 3.18 shows a plot of ferrocene coverage versus time for bpy-supported Ni(II) complexes. A rapid increase in coverage is observed in the first 60 minutes, followed by a much slower increase near the end of the reaction. The reaction is complete after three hours, and extension of the reaction time to 24 hours did not improve the surface coverage of the ferrocene species. Figure 3.18 also shows the linearization of the kinetic data, in which the pseudo-first order rate constant was obtained from the slope of the fitted line. The average rate constant obtained for bpy-based initiators
was \(5.0 \times 10^{-4} \text{ s}^{-1}\), which was roughly five times greater than dppe- \((9.8 \times 10^{-5} \text{ s}^{-1})\) and dppp- \((1.5 \times 10^{-4} \text{ s}^{-1})\) based initiators (Figures 3.19 and 3.20, respectively). First, the difference observed in the cross-coupling reaction rate between bpy and diphosphino-based initiators provides indirect evidence that the ligand exchange reaction has occurred. Secondly, this large rate difference with bpy-based initiators over dppe- and dppp-based initiators is presumably due to the increase in steric effects accompanied with dppe and dppp, which have four bulky phenyl groups (two per phosphine). The steric argument is based on the assumption that transmetallation is the rate-limiting step in the cross-coupling reaction. It should be noted that the electronic effects are also different between bpy and the two bidentate phosphines. With the current experiments it remains undetermined whether transmetallation or reductive elimination is rate limiting in this surface reaction.

**Figure 3.18.** a) Plot of ferrocene coverage vs. time for bpy-based initiator via 1 on gold. b) Linearization of the data to obtain a pseudo-first order rate constant \((5.0 \times 10^{-4} \text{ s}^{-1})\) for the cross-coupling reaction.
Figure 3.19. a) Plot of ferrocene coverage vs. time for dppe-based initiator via 1 on gold. b) Linearization of the data to obtain a pseudo-first order rate constant \((9.8 \times 10^{-5} \text{ s}^{-1})\) for the cross-coupling reaction.

Figure 3.20. a) Plot of ferrocene coverage vs. time for dppp-based initiator via 1 on gold. b) Linearization of the data to obtain a pseudo-first order rate constant \((1.5 \times 10^{-4} \text{ s}^{-1})\) for the cross-coupling reaction.

**Effect of LiCl.** Addition of LiCl has been shown to increase the rate of Mg/halogen exchange due to the ability of LiCl to break up Grignard aggregates.\(^{56}\) Lithium chloride has also been used during polymerization, as it yields polymers with higher molecular weight and lower polydispersity.\(^{57}\) Lohwasser *et al.* observed
higher molecular weight P3HT using LiCl within the same time frame compared to polymerization without LiCl. This was attributed to a calculated 17% reaction rate increase. In addition, LiCl increased reactivity of the sterically hindered isomer. Lanni et al. showed that with dppe as the ligand, reductive elimination is rate limiting, where LiCl would have no acceleration effect, in contrast to the findings of Lohwasser with dppp. With respect to surface coupling reactions, we investigated the dependence of the rate constant of the cross-coupling reaction on the presence of LiCl using SAMs of on gold. An increased rate would provide direct evidence that transmetallation is the rate-limiting step for the surface reaction. Figure 3.21 shows the ferrocene coverage vs. time in the presence of LiCl for all ligands. There is a rapid initial increase in surface coverage followed by a significant decrease over reaction time. The contact angle of the surfaces also decreased with reaction time from ~78° to ~65°, and CV revealed the formation of large pinhole defects in the monolayer (Figure 3.22). We speculate that this “turbo Grignard” is destructive toward Au-S bonds of the alkanethiol monolayers, even at low concentration (0.02 M). Increasing the concentration of the Grignard without LiCl from 0.02 M to 0.1 M had a similar effect on the ferrocene coverage, signifying that a high concentration of Grignard is also not compatible with alkanethiol monolayers.
Figure 3.21. Ferrocene coverage vs. time with LiCl additive via Dppp-, dppe-, and bpy-based initiators using SAMs of 1.

Figure 3.22. CV of bpy-based initiator substrate after LiCl complexed capping agent reaction in presence of aqueous electrode composed of 1 mM K₃Fe(CN)₆ in 0.1M KCl. Over time, pinholes form in the monolayer due to destructive nature of the LiCl Grignard species, as demonstrated by the appearance of K₃Fe(CN)₆ redox peaks.
**Preparation of poly(3-methylthiophene) films via SI-KCTP initiators.**

The surface bound diphosphine-supported (aryl)Ni(II)-Br initiators allow for SI-KCTP on a variety of substrates (Figure 3.23). To demonstrate the effectiveness, a 3-methylthiophene building block was utilized in this work. The methyl substituent in the 3-position of the thiophene ring helps to stabilize the intermediate nickel species without a large steric influence. Previous literature reports of KCTP have demonstrated the necessity of an alkyl substituent.\textsuperscript{58, 59} Beryozkina et al. reported that monomers having alkyl substituents in the 3-position exhibited superior chain growth performance over monomers that lacked an alkyl substituent.\textsuperscript{58} Boyd et al. demonstrated that a substituent in the 3-position is necessary to promote chain-growth character.\textsuperscript{59} The advantage is two-fold: (1) the complex is more inert to disproportionation reactions due to steric blocking of an axial coordination site and (2) ortho substituents hold the plane of the aryl group vertical to the plane of the Ni complex which increases its stability due to interaction between the aryl $\pi^*$ and Ni $d_{\text{xy}}$ orbitals.\textsuperscript{60}

![Figure 3.23. SI-KCTP of poly(3-methylthiophene) using surface bound (aryl)Ni(II)-Br initiators via 6 on SiO$_x$.](image)

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To conduct SI-KCTP, the surface bound diphosphine-supported (aryl)Ni(II)-Br initiators are rinsed after the ligand exchange step and subsequently placed in a solution of monomer under mild stirring. After overnight stirring, substrates are removed from the reaction medium and extensively rinsed with isopropanol, chloroform, and water followed by a fifteen-minute sonication procedure in chloroform and water. It is important to note that polymer is always observed in solution, demonstrating a deviation from the ideal chain-growth nature typically observed with KCTP. Polymerization of P3MT on SiO₂ surfaces yielded reproducible film thicknesses between 40 and 65 nm as measured by ellipsometry. The films do not delaminate from the substrate after sonication in any solvent or a Scotch tape peel test, further signifying the covalent attachment of the P3MT chains. It is important to note that during all SI-KCTP trials, a control substrate containing the same aryl-bromide monolayer, but without the catalyst immobilization step, was used in conjunction with the test substrate. No polymer is observed on control substrates in all polymerization trials, ruling out the possibility of physisorbed polymer. In addition, experiments to unequivocally prove the absence of physisorbed Ni(0) were performed. An alkanethiol monolayer (no aryl bromide present) was exposed to catalyst, rinsed, and placed in a solution of monomer. No conversion of monomer was observed, even after overnight stirring.
**Figure 3.24.** AFM topography images of P3MT films on Si/SiO$_2$ formed from SAMs of 6. 5 μm AFM topography image of P3MT film via a) dppe-based initiators. b) dppp-based initiators. c) dppb-based initiators.

**Figure 3.25.** AFM topography images of P3MT films on Si/SiO$_2$ formed from SAMs of 6. 2 μm AFM topography image of P3MT film via a) dppe-based initiators. b) dppp-based initiators. c) dppb-based initiators.

**Characterization of P3MT films.** Although different initiator densities among the various ligands were observed using the ferrocene “capping agent” described above, the resulting morphology of the P3MT films remained consistent no matter which diphosphine-supported (aryl)Ni(II)-Br initiator was used. Figure 3.24 shows a 5 μm AFM topography images of 65 nm P3MT films fabricated with dppe-, dppp-, and dppb-based initiators on Si/SiO$_2$ (2 μm topographic images are
shown in Figure 3.25). The RMS roughness of the films shown in Figure 3.24 was calculated to be 12-14 nm. This is considerably smoother than films of poly(thiophenes) fabricated in a previous report using monodentate PPh₃ ligands – which may give rise to earlier termination and increased polydispersity of tethered chains.²⁰ The consistent morphology observed on silicon via dppe, dppp, and dppb indicates that the nature of the ligand (and the initiator densities) does not significantly affect the uniformity of P3MT chains. In addition, P3MT was also grafted from ITO surfaces using SAMs of 3. The resulting films also displayed a consistent, uniform morphology similar to that of silicon, despite the fact that ITO is a considerably rougher substrate (Figure 3.26).

**Figure 3.26.** 2 μm AFM topography image of P3MT on ITO using SAMs of 3.
Figure 3.27. a) Representative UV-Vis spectra of 33 nm P3MT film prepared on ITO starting with SAMs of 4. b) Corresponding cyclic voltammogram of the film using ITO as the working electrode.

Figure 3.27 shows the dry state UV-Vis spectra of a 33 nm P3MT on ITO. The absorption onset occurs at 650 nm with a $\lambda_{\text{max}} = 450$ nm. The $\lambda_{\text{max}}$ is considerably lower than reports of poly(3-hexylthiophene) in the dry state.\(^{19}\) This lower $\lambda_{\text{max}}$ can be attributed to the presence of oligomeric material resulting from early chain termination. The appearance of fine structure at 605 nm and 545 nm is indicative of $\pi-\pi$ stacking, and is characteristic of regioregular poly(3-alkylthiophenes).\(^{61}\) Figure 3.27 also shows the resulting cyclic voltammogram of the same P3MT film on ITO as the working electrode. Sharp doping/dedoping waves are apparent, with an anodic peak ($E_{\text{pa}}$) occurring at 0.78 V/SCE and an oxidation pre-wave occurring at 0.4 V/SCE. These doping/dedoping peaks are considerably sharper than electropolymerized films of P3MT, due to well-defined P3MT chains and the absence of crosslinking defects inherent in electrochemical polymerization.

Polarized UV-Vis spectroscopy was also used to probe the structural anisotropy of the P3MT thin films on glass (Figure 3.28). By varying the angle of
incidence and the polarization of light, differences in the absorbance maximum due
to orientation can be observed. The electric field is parallel (p-polarization) and
perpendicular (s-polarization) to the plane of the substrate. An angle of incidence of
0° (from surface normal) showed no difference in the shape and position of the
absorption bands when changing the polarization mode. This implies that the
conjugated backbone of the P3MT chains are oriented randomly about the plane of
the substrate. In the case of spectra recorded at 45°, an absorbance difference in p-
and s-polarized light was observed for films formed from all different initiator
combinations, indicating a modest degree of orientation, likely due to the low
initiator density that forces a deviation from highly stretched polymer chains.
Figure 3.28. Polarized UV-Vis of a 10 nm P3MT film on glass via dppe-based initiators (top), dppp-based initiators (middle), and dppb-based initiators (bottom) using SAM of 5.
Figure 3.29. FTIR spectra of a P3MT film on via 6 on SiO₂. The inset displays the control substrate (left) and test substrate (right).

Figure 3.29 shows the GATR-FTIR spectrum of a 40 nm P3MT film grafted from a dppe-based initiator on silicon wafer. The absorbances visible are aliphatic C-H stretching at 2964, 2933, and 2855 cm⁻¹, and a weak aromatic C-H stretch at 3059 cm⁻¹. Aromatic C-H asymmetric stretches are observed at 1513 and 1458 cm⁻¹, as well as the C-H symmetric stretch at 1437 cm⁻¹. A strong C-H out of plane bending mode observed at 817 cm⁻¹ as well as an in plane bending at 1029 cm⁻¹. The inset is an image of a 40 nm P3MT film along with the corresponding control substrate. P3MT films display a reproducible red color uniformly across the substrate.
Conclusion

In summary, a versatile method for fabricating SI-KCTP initiators on a variety of planar substrates incorporating bidentate phosphine ligands has been demonstrated. Indirect evidence of interfacial disproportionation reactions was observed electrochemically through the use of an aryl organomagnesium ferrocene probe. With respect to all SAMs studied, incorporation of a methyl substituent ortho to the halogen on the thiophene ring helps prevent disproportionation, however an overall lower yield of initiators was observed due to the reduced packing density of SAMs containing the bulky methyl substituent. Initiators formed with phosphonic acids anchor groups did not demonstrate any significant disproportionation reactions among the bidentate phosphine ligands used in this study, since molecules on ITO are not as densely packed as SAMs formed on Au. The use of LiCl or high concentration of Grignard reagent was incompatible with alkanethiol monolayers. The aryl(Ni(II)-Br monolayers were then used to fabricate poly(3-methylthiophene) films on SiO₂ and ITO surfaces. Uniform P3MT films with thicknesses between 40 and 65 nm were characterized using a variety of techniques. Studies using these films as modified interfaces in organic electronics are now possible and currently underway in our laboratory.
References


CHAPTER 4

EFFECT OF SUBSTITUENT LOCATION AND HALIDE TYPE ON THE FIRST
IRREVERSIBLE STEP IN OXIDATIVE ADDITION OF ZEROVALENT NICKEL TO
HALOARENES

Abstract

Mechanistic studies of the Ni-catalyzed Kumada coupling reaction are carried out through analysis of kinetic isotope effects (KIE). It was found that the first irreversible step of the coupling reaction is dependent on the substrate type. Chlorotoluene substrates exhibit an FIS characteristic of π-complexation, where on the other hand, bromotoluene and bromothiophene derivatives exhibit either π-complexation or C-Br bond cleavage at the FIS, which is dependent on the position of the substituent. The results in this report give further insight into oxidative addition processes, which has been a debated mechanism in the last 40 years, as well as rationalize observations in Kumada Catalyst-Transfer Polycondensation.
Introduction

The nickel-catalyzed cross-coupling reaction (Kumada-Corriu) has become widespread for its use in the formation of carbon-carbon bonds in small molecule synthesis. In such reactions, the nickel species undergo a fundamental catalytic cycle involving oxidative addition (OA), transmetallation, and reductive elimination (RE), where each RE step yields a carbon-carbon bond and regenerates active Ni(0). The oxidative addition step represents one of the most basic transformations in organometallic chemistry, where its importance plays a key role in the conversion of starting materials to reactive intermediates. In this oxidative addition step, it is well known that the formal charge on the zerovalent metal increases. It has been proposed by Kochi that the mechanism of oxidative addition of Ni(0) species to aryl halides occurs through a concerted or radical chain process, which can involve the formation of Ni(I) intermediates. It was found that the aryl halogen bond strength was a critical factor in the relative formation of Ni(I) and Ni(II) intermediates and proposed that the oxidative addition products are derived from a common [Ni(I)Ar-X•] precursor. It is clear that further studies are necessary to understand the mechanism of oxidative addition of Ni(0).

This nickel-mediated reaction has also found use in conjugated polymer (CP) synthesis in the last decade, where near monodisperse CPs can be fabricated using Kumada Catalyst-Transfer Polycondensation (KCTP). In KCTP, much research effort has been focused on the generation of external initiators, where a reactive Ni(0) species is mixed with an aryl halide to generate (aryl)Ni(II)-X. Such external initiators are used to extend the capabilities of KCTP, for example, surface-
immobilized external initiators can be used to generate CP brushes.\textsuperscript{9-14} Using Kinetic Isotope Effect (KIE) studies, the first irreversible step (FIS) of Ni(0) OA to haloarenes has been demonstrated to be $\pi$-complexation.\textsuperscript{15} In contrast, when Pd(0) catalysts are used, the FIS is the C-Br bond cleavage step itself with no prior $\pi$-complexation. The difference in the $d$-electron donating ability of the two metals was used to rationalize the results.

In the context of KCTP, we were interested in understanding the OA mechanism when the aliphatic substituent is \textit{para} to the halide, since such \textit{para}-substituents are used as tethers on surfaces and spherical particles to generate CP brushes.\textsuperscript{10,12} In addition to understanding the role of substituents, the effect of the halide is also important to consider. Substrates incorporating a bromide have largely different energetic profiles that those incorporating a chloride. In the report by Nakamura and coworkers, the aliphatic substituent is \textit{ortho} to the halide for all reactions. The influence of the substituent location (\textit{meta} and \textit{para} substituted aryl halides) on the ring has not yet been investigated. A series of thiophene derivatives are also investigated to further understand Ni(0) interactions with aromatic rings that contain a heteroatom, which has also not yet been reported to date. Such derivatives are commonly used in KCTP as both a monomer and initiator structure.

A previous report\textsuperscript{10} by our group regarding the yield of Ni(0) OA with surface tethered aryl halides speculated two important points: 1) disproportionation is a major side reaction between surface-bound (aryl)Ni(II)-Br sites and 2) placing a substituent \textit{ortho} to the aryl halogen bond reduces such side reactions, but comes at a cost of reduced OA yield. This reduced yield was surprising to us, considering such
complexes in solution can be obtained near quantitatively.\textsuperscript{16,17} In the context of surface-tethered aryl halides, it was speculated that ortho-substituents block the approach of the Ni(0) catalyst, thus limiting OA to generate the (aryl)Ni(II)-Br species necessary for surface-initiated polymerization. To further investigate the nature of this steric effect, an array of aryl halides are coupled with aryl or alkyl magnesium halides using dppp-ligated nickel catalysts. The $^{13}$C/$^{12}$C ratio is obtained after recovery of unreacted starting material through quantitative $^{13}$C NMR analysis and the corresponding KIE values are calculated. The KIE is dependent on the change in vibrational modes due to the mass change of an atom by isotopic labeling. In this case, deliberate labeling is unnecessary as NMR can easily measure the abundance of $^{13}$C in a molecule. The change of vibrational modes works to lower the zero point vibrational energy (ZPE) of the stationary state of the heavier molecule, while the ZPE of the transition state remains relatively unchanged. This leads to a larger activation barrier for the isotopically labeled molecules, and reactions of heavier isotopes are kinetically slowed. Thus, reaction with substrates containing the lighter atom ($^{12}$C) will preferentially react and starting material containing the heavier atom ($^{13}$C) will be left behind. The KIE ratio will be increased if an atom is involved in the FIS.\textsuperscript{18} This investigation can give further insight into Ni(0) interactions with haloarenes, where such Ni(0) interactions lead to the chain-growth character of KCTP and may also play an important role in the fabrication of KCTP external initiators.
Experimental

Procedure for determination of KIE. All samples were prepared with 4M analyte and 0.1M Cr(acac)$_3$ for NMR ($^{13}$C observe at 125.721 MHz and $^1$H decouple at 500 MHz). $T_1$ analysis was performed with each sample prior to NMR analysis. The nucleus with the longest $T_1$ in the material was used to calculate the relaxation delay (5×$T_1$). 4000-5000 scans were performed on each sample using the inverse gated decoupling technique (No NOE) with a Waltz-16 decoupling sequence for $^1$H. The pulse width was set at 90°. To ensure consistent decoupling across the entire spectrum, the sweep width was adjusted to 195 downfield and -35 upfield. All spectra were zero filled to 256k points prior to Fourier transformation. Manual phasing and automatic baseline correction were applied. Integrations were performed from 5 Hz on both sides of the peak center. Integrations did not include $^{13}$C satellites. The signal-to-noise ratio for all spectra was at least 1000.

KIE Calculations with all standard deviations. Values for $R_0$, $R$, and KIE were obtained as an average of 3 integrations. The spectra were Fourier transformed, phased, and baselined prior to integration. This ensured the standard deviation measured included any differences in phasing, baseline correction, and integration processes.

$$KIE_{exp} = \frac{\ln(1-f)}{\ln\left(\frac{(1-f)R}{R_0}\right)}$$

Synthesis of 2-bromo-3-methylthiophene. See previous procedures.$^{10}$

Synthesis of 2-bromo-5-methylthiophene. To a 3-neck flask fitted with an addition funnel was added thiophene (200 mmol) and 200 mL of THF. This was
cooled to -78 °C followed by the addition of nBuLi drop-wise (200 mmol, 125 mL). The reaction was stirred at -78 °C for one hour. Mel (240 mmol, 34.05 g) was added to the addition funnel and added drop-wise over the course of one hour, keeping the reaction at -78 °C. After complete addition, the reaction was allowed to warm to room temperature overnight. The reaction was poured into water and extracted with hexanes, washed with water 3x, and dried over MgSO₄. The crude material was flashed through an alumina plug with hexanes to yield 9.76 g 2-methylthiophene as a colorless oil (51%). ¹H NMR (CDCl₃): 7.081 (dd, 1H, J=5.3 Hz), 6.9 (t, 1H, J=4.3 Hz), 6.76 (dd, 1H), 2.505 (s, 3H). To a one neck flask containing 200 mL DMF was added 2-methylthiophene (183.1 mmol, 17.98 g) and recrystallized NBS (183.1 mmol, 32.58 g). After stirring for 24 h, the reaction was poured into water and extracted with hexanes, washed with water 3x, and dried over MgSO₄. The crude product was distilled to yield 31 g pure 2-bromo-5-methylthiophene as a colorless oil (97%). ¹H NMR (CDCl₃, 300 MHz) δ (ppm): 6.829 (d, 1H, J=3.7 Hz), 6.52 (dd, 1H, J=3.7 Hz), 2.42 (s, 3H).

**Synthesis of 2-bromo-5-propylthiophene.** To a solution of thiophene (200 mmol) in 200 mL THF at -78 °C was added nBuLi (200 mmol, 125 mL). This was stirred at -78 °C for 1 h followed by the drop-wise addition of bromopropane (220 mmol, 27 g). The reaction was allowed to warm to room temperature overnight. The following day, the reaction was poured into ice water and extracted with diethyl ether, washed with water 3x, brine 3x, and dried over MgSO₄. After removal of solvent, the crude product was distilled at 115 °C to yield 18.28 g pure 2-propylthiophene (72.5%). ¹H NMR (CDCl₃): 7.109 (d, 1H, J=5.2 Hz), 6.92 (t, 1H, J=4.3 Hz), 6.78 (d, 1H, J=2.7 Hz).
Hz), 2.804 (t, 2H, J=7.7 Hz), 1.706 (m, 2H, J=7.5 Hz), .979 (t, 3H, J=7.4 Hz). To a one neck-flask was added 2-propylthiophene (15.5 g, 122.8 mmol) in 150 mL DMF. Recrystallized NBS (21.85 g, 122.8 mmol) was added in one portion and the reaction was stirred overnight. The reaction was poured into water and extracted with hexanes, washed with water 3x, and dried over MgSO₄. After solvent removal, the product was distilled (51 °C @ 1 torr) to yield 24.33 g pure 2-bromo-5-methylthiophene as a colorless oil (96%).

\[\text{1H NMR (CDCl}_3\text{, 300 MHz)} \delta (\text{ppm}): 6.842 (d, 1H, J=3.7 Hz), 6.533 (d, 1H, J=3.6 Hz), 2.718 (t, 2H, J=7.4 Hz), .958 (t, 3H, J=7.4 Hz).\]

Synthesis of 8-(5-chlorothiophene-2-yl)octane-t-thiol. The synthesis of 2-(8-bromooctyl)thiophene is reported elsewhere.¹⁰ To a solution of 2-(8-bromooctyl)thiophene (10 mmol, 2.75 g) in 20 mL DMF was added NCS (1.46 g, 11 mmol) at room temperature. The reaction was stirred 24 h. The reaction was poured into ice water, extracted with hexane, dried over MgSO₄, filtered, and concentrated. The concentrated was flashed through a column of silica gel using hexanes as the eluent to yield 1.92 g 5-chloro-2-(8-bromooctyl)thiophene (60%).

\[\text{1H NMR (CDCl}_3\text{, 300 MHz)} \delta (\text{ppm}): 6.69 (d, 1H, J=3.9 Hz), 6.52 (d, 1H, J=3.6 Hz), 3.99 (t, 2H, J=7.0 Hz), 2.71 (t, 2H, J=7.7 Hz), 1.85 (p, 2H, J=8.5 Hz), 1.3 (m, 8H).\]

To an argon purged 3-neck flask fitted with a reflux condenser was added 5-chloro-2-(8-bromooctyl)thiophene (2.18 g, 6.15 mmol), thiourea (1.17 g, 15.37 mmol) and 100 mL of degassed ethanol. The reaction was refluxed overnight. The reaction was cooled to room temperature and 30 mL of 1M NaOH was added. The reaction was refluxed for an additional 4 h, cooled to room temperature, and brought to neutral pH with dilute HCl. The solvent was removed,
diluted with DCM, washed with brine 3x, dried over MgSO$_4$, filtered, and concentrated. The concentrated was flashed through a column of silica gel using 1:10 EtOAc:Hex as the eluent to yield 1.5 g 8-(5-chlorothiophene-2-yl)octane-1-thiol (70%). $^1$H NMR (CDCl$_3$, 300 MHz) $\delta$ (ppm): 6.94 (d, 1H, J=3.7Hz), 6.525 (d, 1H, 3.9 Hz), 2.706 (t, 2H, J=7.6 Hz), 2.515 (q, 2H, J=7.5 Hz), 1.61 (m, 4H), 1.2-1.5 (m, 9H).

**KIE reaction of 2-bromo-3-methylthiophene with thienyl magnesium chloride.**

To a 3-neck flask containing 2-bromothiophene (92.8 mmol, 15.12 g) in 100 mL THF was added isopropylmagnesium chloride (92.8 mmol, 46.4 mL) drop-wise at 0 °C. After complete conversion as indicated by TLC, the resulting solution of 2-thienylmagnesium chloride was transferred to an addition funnel fitted to a flask containing 2-bromo-3-methylthiophene (92.8 mmol, 16.44 g) and 3 mol % Ni(dppp)Cl$_2$ in 100 mL THF at 0 °C. This was stirred overnight at room temperature. The next day, the reaction was quenched with 1 M HCl and the solvent was removed under vacuum. The crude mixture was dissolved in hexanes and washed with water 3x, dried over MgSO$_4$, and concentrated. Crude NMR showed near quantitative target product with a small amount of 2-bromo-3-methylthiophene. Distillation yielded 125 mg (98% conversion) starting material followed by cross-coupled product (55 °C, 200 mtorr) to yield 12.93 g (80%). $^1$H NMR (CDCl$_3$, 300 MHz) $\delta$ (ppm): 7.298 (dd, 1H, J=5 Hz), 7.145 (m, 2H), 7.069 (t, 1H, J=4.7 Hz), 6.892 (d, 1H, J=5 Hz), 2.397 (s, 3H).
Table 4.1. Integral values before and after reaction followed by corresponding KIE values for 2-bromo-3-methylthiophene.

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</table>

KIE reaction of 2-bromo-5-methylthiophene with thienyl magnesium chloride.

To a solution of 2-bromothiophene (175 mmol, 28.53 g) in 100 mL THF was added isopropylmagnesium chloride (175 mmol, 87.93 mL) drop-wise at 0 °C. This was stirred for 2 h and TLC indicated complete conversion to thienyl magnesium chloride. This solution was transferred to an addition funnel fitted to a 3-neck flash via cannula. The solution was added drop-wise to 2-bromo-5-methylthiophene (175 mmol, 30.98 g) and 3 mol% Ni(dppp)Cl₂ in 140 mL THF at 0 °C. This was stirred 48 h. The reaction was quenched with dilute HCl followed by removal of the solvent. The crude mixture was dissolved in hexane and washed with water 3x, brine 3x, and dried over MgSO₄. Integration of crude NMR indicated target product as the main component along with 2,2'-dimethyl-2,2'-bitihophene, bitiophene, and starting material. The starting material was distilled off to yield 6.4 g (80% conversion).
Table 4.2. Integral values before and after reaction followed by corresponding KIE values for 2-bromo-5-methylthiophene.

<table>
<thead>
<tr>
<th>Carbon</th>
<th>R₀</th>
<th>R</th>
<th>KIE</th>
</tr>
</thead>
<tbody>
<tr>
<td>*</td>
<td>1000.00 ± 0</td>
<td>1000.00 ± 0</td>
<td>N/A</td>
</tr>
<tr>
<td>2</td>
<td>1243.4067 ± 0.3868</td>
<td>1257.25 ± 0.5543</td>
<td>1.0069 ± 0.0002</td>
</tr>
<tr>
<td>3</td>
<td>1102.1233 ± 1.0904</td>
<td>1104.73 ± 0.5543</td>
<td>1.0015 ± 0.0006</td>
</tr>
<tr>
<td>4</td>
<td>1102.97 ± 0.4151</td>
<td>1101.2933 ± 0.4952</td>
<td>0.9991 ± 0.0005</td>
</tr>
<tr>
<td>5</td>
<td>1185.0867 ± 0.3758</td>
<td>1183.35 ± 0.4151</td>
<td>0.9991 ± 0.0002</td>
</tr>
</tbody>
</table>

KIE reaction of 2-bromo-5-propylthiophene with thienyl magnesium chloride.

In a pear shaped 3-neck flask containing a solution of 2-bromothiophene (87 mmol, 14.18 g) in 100 mL THF was added isopropylmagnesium chloride (87 mmol, 43.5 mL) drop-wise at 0 °C. This was stirred for 2 h and TLC indicated complete conversion to thienyl magnesium chloride. This solution as transferred to a drop funnel fitted to a 3-neck flash via cannula. The solution was added drop-wise to 2-bromo-5-propylthiophene (87 mmol, 17.84 g) and 3 mol % Ni(dppp)Cl₂ in 100 mL THF at 0 °C. This was stirred 48 h. The reaction was quenched with 1 M HCl followed by removal of the solvent under vacuum. The crude mixture was dissolved in hexane and washed with water 3x, dried over MgSO₄, and concentrated. Crude NMR indicated the target product as the main component, as well as unreacted starting material and 2,2'-dipropyl-2,2’bithiophene, and bithiophene, which were not separated. The starting material was recovered via distillation to yield 4.86 g (73% conversion).
Table 4.3. Integral values before and after reaction followed by corresponding KIE values for 2-bromo-5-propylthiophene.

<table>
<thead>
<tr>
<th>Carbon</th>
<th>R0</th>
<th>R</th>
<th>KIE</th>
</tr>
</thead>
<tbody>
<tr>
<td>*1</td>
<td>1000.00 ± 0</td>
<td>1000.00 ± 0</td>
<td>N/A</td>
</tr>
<tr>
<td>*2</td>
<td>1025.9467 ± 0.3926</td>
<td>1027.51 ± 0</td>
<td>1.0012 ± 0.0003</td>
</tr>
<tr>
<td>*3</td>
<td>958.9833 ± 0.3695</td>
<td>961.38 ± 0</td>
<td>1.0019 ± 0.0003</td>
</tr>
<tr>
<td>2</td>
<td>1144.3433 ± 0.4388</td>
<td>1161.8233 ± 0.475</td>
<td>1.0117 ± 0.0006</td>
</tr>
<tr>
<td>3</td>
<td>965.2367 ± 0.65</td>
<td>967.14 ± 0</td>
<td>1.0015 ± 0.0005</td>
</tr>
<tr>
<td>4</td>
<td>1040.0733 ± 0.4561</td>
<td>1046.3567 ± 0.2309</td>
<td>1.0046 ± 0.0005</td>
</tr>
<tr>
<td>5</td>
<td>1136.9267 ± 0.475</td>
<td>1139.2533 ± 1.3106</td>
<td>1.0016 ± 0.0008</td>
</tr>
</tbody>
</table>

**KIE reaction of o-chlorotoluene with hexylmagnesium bromide.** In a pear shaped 3-neck round bottom flask equipped with a reflux condenser containing magnesium metal (145 mmol, 3.53 g) in 100 mL diethyl ether was added 1-bromohexane (144 mmol, 23.75 g) drop-wise. The solution was maintained at reflux during the entire addition of 1-bromohexane. The solution was stirred an additional hour (near all of the magnesium metal was consumed) and then transferred via cannula to an addition funnel connected to a 3-neck round bottom flask containing o-chlorotoluene (120 mmol, 15.19 g) and 2 mol % Ni(dppp)Cl₂ at 0 °C. The hexylmagnesium bromide solution was then added drop-wise. The reaction was stirred 24 h at room temperature after complete addition. The following day, the reaction was slowly quenched with 1 M HCl, poured into a separatory funnel, and washed 3x with water, 3x with brine, and dried over MgSO₄. The starting material was recovered in a cold trap via distillation to yield 1.52 g (90% conversion). The amount of pure product obtained via distillation was 16.40 g (78%).¹H NMR (CDCl₃, 300 MHz) δ (ppm): 7.12 (m, 3H), 2.59 (t, 2H, J=7.9 Hz), 2.31 (s, 3H), 1.56 (p, 2H, J=7.6 Hz), 1.34 (m, 6H), 0.90 (t, 3H, J=6.5 Hz).
Table 4.4. Integral values before and after reaction followed by corresponding KIE values for o-chlorotoluene.

<table>
<thead>
<tr>
<th>Carbon</th>
<th>R₀</th>
<th>R</th>
<th>KIE</th>
</tr>
</thead>
<tbody>
<tr>
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<td>1191.6967 ± 0.7217</td>
<td>0.9981 ± 0.0003</td>
</tr>
<tr>
<td>2</td>
<td>1172.82 ± 0</td>
<td>1195.2667 ± 0.7217</td>
<td>1.0083 ± 0.0003</td>
</tr>
<tr>
<td>3</td>
<td>1024.51 ± 0</td>
<td>1071.8433 ± 0.6466</td>
<td>1.02 ± 0.0003</td>
</tr>
<tr>
<td>4</td>
<td>1047.7267 ± 0.5774</td>
<td>1058.4433 ± 0.9906</td>
<td>1.0044 ± 0.0002</td>
</tr>
<tr>
<td>5</td>
<td>1062.55 ± 0</td>
<td>1073.8933 ± 1.1836</td>
<td>1.0046 ± 0.0005</td>
</tr>
<tr>
<td>6</td>
<td>1046.45 ± 0</td>
<td>1050.7267 ± 0.6351</td>
<td>1.0018 ± 0.0003</td>
</tr>
</tbody>
</table>

KIE reaction of m-chlorotoluene with hexylmagnesium bromide. In a pear shaped 3-neck round bottom flask equipped with a reflux condenser containing magnesium metal (145 mmol, 3.53 g) in 100 mL diethyl ether was added 1-bromohexane (144 mmol, 23.75 g) drop-wise. The solution was maintained at reflux during the entire addition. The solution was stirred an additional hour (near all of the magnesium metal was consumed) and then transferred via cannula to an addition funnel connected to a 3-neck round bottom flask containing m-chlorotoluene (120 mol, 15.19 g) and 2 mol % Ni(dppp)Cl₂ at 0 °C. The hexylmagnesium bromide solution was then added drop-wise. The reaction was stirred 24 h at room temperature after complete addition. The following day the reaction was slowly quenched with 1 M HCl, poured into a separatory funnel, and washed 3x with water, 3x with brine, and dried over MgSO₄. The starting material was recovered in a cold trap via distillation to yield 80 mg (99% conversion). Yield of pure target product was 20.15 g (95%). ¹H NMR (CDCl₃, 300 MHz) δ (ppm): 7.16
(t, 1H, J=8.1 Hz), 6.98 (m, 2H), 2.56 (t, 2H, J=7.9 Hz), 2.33 (s, 3H), 1.6 (p, 2H, J=7.6 Hz), 1.31 (m, 6H), 0.88 (t, 3H, J=6.5 Hz).

Table 4.5. Integral values before and after reaction followed by corresponding KIE values for m-chlorotoluene.

<table>
<thead>
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<th>R</th>
<th>KIE</th>
</tr>
</thead>
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<td>1000.00</td>
<td>N/A</td>
</tr>
<tr>
<td>1</td>
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</tr>
<tr>
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<td>1054.5133 ± 0.5783</td>
<td>1087.3467 ± 0.9804</td>
<td>1.0067 ± 0.0003</td>
</tr>
<tr>
<td>3</td>
<td>1172.1533 ± 0.56</td>
<td>1213.8867 ± 0.3868</td>
<td>1.0077 ± 0.0002</td>
</tr>
<tr>
<td>4</td>
<td>1051.0933 ± 0.4631</td>
<td>1092.52 ± 0</td>
<td>1.0085 ± 0.0001</td>
</tr>
<tr>
<td>5</td>
<td>1064.77 ± 0.4451</td>
<td>1101.73 ± 0</td>
<td>1.0075 ± 0.0001</td>
</tr>
<tr>
<td>6</td>
<td>1063.1667 ± 0.7637</td>
<td>1102.67 ± 0.485</td>
<td>1.008 ± 0.0001</td>
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</tbody>
</table>

KIE reaction of p-chlorotoluene with hexylmagnesium bromide. In a pear shaped 3-neck round bottom flask equipped with a reflux condenser containing magnesium metal (145 mmol, 3.53 g) in 100 mL diethyl ether was added 1-bromohexane (144 mmol, 23.75 g) drop-wise. The solution was maintained at reflux during addition. The solution was stirred an additional hour (near all of the magnesium metal was consumed) and then transferred via cannula to an addition funnel connected to a 3-neck round bottom flask containing p-chlorotoluene (120 mol, 15.19 g) and 2 mole % Ni(dppp)Cl₂ at 0 °C. The hexylmagnesium bromide solution was then added drop-wise. The reaction was stirred 24 h at room temperature after complete addition. The following day the reaction was slowly quenched with dilute HCl, poured into a separatory funnel, and washed 3x with water, 3x with brine, and dried over MgSO₄. The starting material was recovered at a cold trap via distillation to yield 2.23 g (89% conversion). The yield of target
product was 15.82 g (75%). $^1$H NMR (CDCl$_3$, 300 MHz) $\delta$ (ppm): 7.07 (m, 3H), 2.56 (t, 2H, J=8 Hz), 2.315 (s, 3H), 1.58 (p, 2H, J=7.6 Hz), 1.30 (m, 6H), 0.88 (t, 3H, J=6.4 Hz).

<table>
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<th>$R$</th>
<th>KIE</th>
</tr>
</thead>
<tbody>
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<td>1000.00</td>
<td>N/A</td>
</tr>
<tr>
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<td>1191.69 ± 0.8072</td>
<td>1.0013 ± 0.0006</td>
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<tr>
<td>2, 6</td>
<td>2157.82 ± 0</td>
<td>2165.6667 ± 1.6339</td>
<td>1.0019 ± 0.0004</td>
</tr>
<tr>
<td>3, 5</td>
<td>2092.8 ± 0</td>
<td>2159.05 ± 1.6281</td>
<td>1.0167 ± 0.0004</td>
</tr>
<tr>
<td>4</td>
<td>1193.23 ± 0.6235</td>
<td>1209.1333 ± 0.9122</td>
<td>1.007 ± 0.0004</td>
</tr>
</tbody>
</table>

*The KIE values for equivalent carbon atoms were halved prior to assignments in the discussion portion of this chapter.

**KIE reaction of o-bromotoluene with hexylmagnesium bromide.** In a pear shaped 3-neck round bottom flask equipped with a reflux condenser containing magnesium metal (96.8 mmol, 2.35 g) in 80 mL diethyl ether was added 1-bromohexane (96 mmol, 15.83 g) drop-wise. The solution was maintained at reflux during addition. The solution was stirred an additional hour (near all of the magnesium metal was consumed) and then transferred via cannula to an addition funnel connected to a 3-neck round bottom flask containing o-bromotoluene (80 mmol, 13.68 g) and 2 mol % Ni(dppp)Cl$_2$ at 0 °C. The hexylmagnesium bromide solution was then added drop-wise. The reaction was stirred 24 h at room temperature after complete addition. The following day the reaction was slowly quenched with 1 M HCl, poured into a separatory funnel, and washed 3x with water, 3x with brine, and dried over MgSO$_4$. The starting material was recovered via
distillation to yield 3.39 g (83% conversion). Also recovered was toluene (0.90 g). The amount of pure target product obtained after distillation was 7.25 g (52%). 1H NMR (CDCl₃, 300 MHz) δ (ppm): 7.12 (m, 3H), 2.58 (t, 2H, J=8 Hz), 2.30 (s, 3H), 1.55 (p, 2H, J=7.6 Hz), 1.33 (m, 6H), 0.89 (t, 3H, J=6.5 Hz).

<table>
<thead>
<tr>
<th>Carbon</th>
<th>R₀</th>
<th>R</th>
<th>KIE</th>
</tr>
</thead>
<tbody>
<tr>
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<td>1000.00</td>
<td>1000.00</td>
<td>N/A</td>
</tr>
<tr>
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<td>1098.4467 ± 1.136</td>
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<td>1.017 ± 0.0003</td>
</tr>
<tr>
<td>2</td>
<td>1092.01 ± 1.4501</td>
<td>1106.82 ± 1.7967</td>
<td>1.0098 ± 0.0022</td>
</tr>
<tr>
<td>3</td>
<td>1048.92 ± 0.6478</td>
<td>1066.0233 ± 1.2</td>
<td>1.0118 ± 0.0008</td>
</tr>
<tr>
<td>4</td>
<td>1028.4467 ± 1.8029</td>
<td>1039.66 ± 2.5993</td>
<td>1.0079 ± 0.0031</td>
</tr>
<tr>
<td>5</td>
<td>1028.8667 ± 5.9884</td>
<td>1042.4667 ± 2.5419</td>
<td>1.0096 ± 0.006</td>
</tr>
<tr>
<td>6</td>
<td>1015.11 ± 1.1972</td>
<td>1028.1467 ± 0.4126</td>
<td>1.0093 ± 0.0011</td>
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</tbody>
</table>

KIE reaction of m-bromotoluene with hexylmagnesium bromide. In a pear shaped 3-neck round bottom flask equipped with a reflux condenser containing magnesium metal (96.8 mmol, 2.35 g) in 80 mL diethyl ether was added 1-bromohexane (96 mmol, 15.83 g) drop-wise. The solution was maintained at reflux during entire addition. The solution was stirred an additional hour (near all of the magnesium metal was consumed) and then transferred via cannula to an addition funnel connected to a 3-neck round bottom flask containing m-bromotoluene (80 mmol, 13.68 g) and 2 mol % Ni(dpdp)Cl₂ at 0 °C. The hexylmagnesium bromide solution was then added drop-wise. The reaction was stirred 24 h at room temperature after complete addition. The following day the reaction was slowly quenched with 1M HCl, poured into a separatory funnel, and washed 3x with water,
3x with brine, and dried over MgSO₄. The starting material was recovered via distillation to yield 1.97 g (85% conversion). The amount of pure target product obtained was 7.5 g (53%). ¹H NMR (CDCl₃, 300 MHz) δ (ppm): 7.16 (t, 1H, J=8.1 Hz), 6.98 (m, 2H), 2.56 (t, 2H, J=7.9 Hz), 2.33 (s, 3H), 1.6 (p, 2H, J=7.6 Hz), 1.3 (m, 6H), 0.88 (t, 3H, J=6.5 Hz).

Table 4.8. Integral values before and after reaction followed by corresponding KIE values for m-bromotoluene.

<table>
<thead>
<tr>
<th>Carbon</th>
<th>R₀</th>
<th>R</th>
<th>KIE</th>
</tr>
</thead>
<tbody>
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<td>*</td>
<td>1000.00</td>
<td>1000.00</td>
<td>N/A</td>
</tr>
<tr>
<td>1</td>
<td>1066.4467 ± 0.6853</td>
<td>1065.5833 ± 0.5832</td>
<td>0.9996 ± 0.0006</td>
</tr>
<tr>
<td>2</td>
<td>996.4 ± 0.3727</td>
<td>1002.41 ± 0.5758</td>
<td>1.0032 ± 0.0002</td>
</tr>
<tr>
<td>3</td>
<td>1058.55 ± 0.6843</td>
<td>1073.41 ± 1.5239</td>
<td>1.0074 ± 0.001</td>
</tr>
<tr>
<td>4</td>
<td>995.6633 ± 0.6992</td>
<td>1004.6267 ± 1.413</td>
<td>1.0047 ± 0.0011</td>
</tr>
<tr>
<td>5</td>
<td>982.2133 ± 0.6469</td>
<td>987.9267 ± 1.2683</td>
<td>1.0031 ± 0.0009</td>
</tr>
<tr>
<td>6</td>
<td>977.37 ± 0.2883</td>
<td>979.2633 ± 2.9707</td>
<td>1.001 ± 0.0018</td>
</tr>
</tbody>
</table>

**KIE reaction of p-bromotoluene with hexylmagnesium bromide.** In a pear shaped 3-neck round bottom flask equipped with a reflux condenser containing magnesium metal (151 mmol, 4.411 g) in 100 mL diethyl ether was added 1-bromohexane (150 mmol, 24.76 g) drop-wise. The solution was maintained at reflux during addition. The solution was stirred an additional hour (near all of the magnesium metal was consumed) and then transferred via cannula to an addition funnel connected to a 3-neck round bottom flask containing p-bromotoluene (125 mol, 21.379 g) and 2 mol % Ni(dppp)Cl₂ at 0 °C. The hexylmagnesium bromide solution was then added drop-wise. The reaction was stirred 24 h after complete addition. The following day the reaction was slowly quenched with 1 M HCl, poured
into a separatory funnel, and washed 3x with water, 3x with brine, and dried over MgSO₄. The starting material was recovered via distillation to yield 7.1 g (67% conversion). Also recovered was toluene (~3 g). The amount of pure target product obtained was 8.6 g (40%). ¹H NMR (CDCl₃, 300 MHz) δ (ppm): 7.07 (m, 3H), 2.56 (t, 2H, J=8 Hz), 2.315 (s, 3H), 1.58 (p, 2H, J=7.6 Hz), 1.30 (m, 6H), 0.88 (t, 3H, J=6.4 Hz).

Table 4.9. Integral values before and after reaction followed by corresponding KIE values for p-bromotoluene.¹

<table>
<thead>
<tr>
<th>Carbon</th>
<th>R₀</th>
<th>R</th>
<th>KIE</th>
</tr>
</thead>
<tbody>
<tr>
<td>*</td>
<td>1000.00</td>
<td>1000.00</td>
<td>N/A</td>
</tr>
<tr>
<td>1</td>
<td>1205.2533 ± 0.7506</td>
<td>1202.7833 ± 0.0751</td>
<td>0.9982 ± 0.0006</td>
</tr>
<tr>
<td>2, 6</td>
<td>2082.03 ± 0</td>
<td>2074.94 ± 0</td>
<td>0.9969 ± 0</td>
</tr>
<tr>
<td>3, 5</td>
<td>2221.67 ± 0.2944</td>
<td>2205.2467 ± 0.3522</td>
<td>0.9934 ± 0.0001</td>
</tr>
<tr>
<td>4</td>
<td>1192.45 ± 0</td>
<td>1202.26 ± 0</td>
<td>1.0074 ± 0</td>
</tr>
</tbody>
</table>

¹The KIE values for equivalent carbon atoms were halved prior to assignments in the discussion portion of this chapter.

**Synthesis of 2-ferrocenyl-5-bromothiophene.** See previous published procedure.¹⁰

**Magnesiation of 2-ferrocenyl-5-bromothiophene.** See previous published procedure.¹⁰

**Formation and characterization of surface-bound (thienyl)Ni(II)-Cl.** In a glovebox, 30 mg of Ni(COD)₂ and 17 mg of 2,2’-bipyridine (bpy) was added to a 10 mL solution of toluene. Upon dissolving, the solution changed a dark purple color characteristic of Ni(COD)bpy. This solution was poured over gold substrates functionalized with 8-(5-chlorothiophene-2-yl)octane-1-thiol. This was allowed to react one hour. Substrates were removed from the Ni(COD)bpy solution, extensively rinsed with THF, and placed in a solution of ferrocene capping agent. This was
allowed to react overnight. The following day, the substrates were removed, rinsed extensively with DCM, water, and ethanol, and dried under a nitrogen stream. The substrates were then subject to electrochemical analysis to determine composition of surface-coupled ferrocene.

Discussion and Results

Initial experiments to obtain quantitative $^{13}$C spectra with a signal-to-noise ratio of at least 1000 to one proved to be time consuming and costly. To allow nuclei to fully relax after each successive pulse requires a delay of at least $5 \times T_1$. With $T_1$ values reaching almost 80 seconds for the aryl halide molecules in this study, it was necessary to shorten the values using a relaxation agent. Other reports have used such agents successfully, however, this strategy has not yet been used for analysis of haloarenes.$^{19, 20}$ When NMR samples were spiked with Cr(acac)$_3$ (0.1 M), $T_1$’s decreased from $\sim$70 s to less than 1 s, which allows for a much shorter pulse delay ($\sim 5 \times T_1$).
Figure 4.1 lists the aryl halides investigated in this study and the corresponding reactions. Both substituent position and halide type are varied. Thienylmagnesium chloride is used as the source of nucleophile in reactions utilizing 3a, 3b, and 3c to minimize magnesium halogen exchange processes that are inherent when using alkyl Grignard reagents, since the rate of magnesium halogen exchange with bromothiophene derivatives are orders of magnitude faster than rates with phenyl bromides. For chloro- and bromotoluene derivatives, the substituent is varied ortho, meta, and para to the halide. In the case of bromothiophene derivatives, the alkyl substituent is placed in either the 3-position or the 5-position.

Figure 4.1. A list of haloarenes used in this study and the corresponding reactions for determination of KIEs.
Figure 4.2. Experimental KIE values of o-chlorotoluene, m-chlorotoluene, and p-chlorotoluene substrates. The FIS is pi-complexation in all cases. Also notable is the drasteric matic influence of the substituent location on KIE values within the haloarene. For all integral values and standard deviations of measurements, see tables 4.4 to 4.6 in the experimental section.

The reaction of 1a with hexylmagnesium bromide yields near quantitative conversion of starting material with no byproducts. The KIE values obtained for 1a indeed demonstrate Ni(0) π-complexation as the FIS on the least hindered side of the ring (Figure 4.2), as shown by $^{13}$C enrichment across multiple carbons in the aromatic ring. The highest KIE value of 1.02 was observed at the carbon in the 3-position. Carbons #1 and #6 demonstrated negligible KIE values of 0.998 and 1.002, respectively. This is reasonable considering the steric effect of the methyl substituent on carbons #1 and #6. Enrichment is also observed at carbon #2, however, it is on par with carbons #4 and #5. The data suggests that the Ni(0) species can complex to the aromatic system as far as carbons #4 and #5, and “ring walk” to the aryl chloride bond. These results are in full agreement with Nakamura and coworkers. Furthermore, reaction of p-chlorotoluene (1c) with hexylmagnesium bromide yields similar results, where π-complexation is the FIS as demonstrated by KIE values at carbons #3, #4, and #5 being 1.008, 1.007, and 1.008, respectively. Carbon atoms #1, #2, and #6 show negligible enrichment in $^{13}$C due to sterics as observed with 1a. Finally, reaction of m-chlorotoluene (1b) with

<table>
<thead>
<tr>
<th>Carbon</th>
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<th>1b KIE</th>
<th>1c KIE</th>
</tr>
</thead>
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<td>1.004</td>
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<td>4</td>
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<td>1.009</td>
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<td>5</td>
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<td>6</td>
<td>1.002</td>
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hexylmagnesium bromide proceeded to near quantitative completion with no side products. KIE values of 1.009-1.010 across carbons #2-6 demonstrate pi-complexation as the FIS. Because of the consistency in observed KIE values around the methyl substituent being negligible regardless of substituent position, it can be safely attributed to a steric effect. The FIS is a π-complexation step for all chlorotoluene derivatives regardless of substituent position.

Figure 4.3. Experimental KIE values of o-bromotoluene, m-bromotoluene, and p-bromotoluene substrates. The FIS is pi-complexation when the substituent is ortho to the bromide. When the substituent is meta or para to the bromide, the FIS is oxidative addition. For all integral values and standard deviations of measurements, see tables 4.7 to 4.9 in the experimental section.

On the other hand, a change of the halogen from chlorine to bromine changes the nature of the FIS so that it is substituent dependent (Figure 4.3). The reaction of o-bromotoluene (2a) with hexylmagnesium bromide yields $^{13}$C enrichment across nearly all carbons in the ring, which implies π-complexation is the FIS as observed with all of the chlorides (1a-1c). On the other hand, reaction of p-bromotoluene (2c) with hexylmagnesium bromide has an FIS characteristic of the C-Br bond cleavage step with no pi-complexation, as demonstrated by sole enrichment in $^{13}$C at the carbon #4 yielding a KIE value of 1.007, where all other carbons remained ~1. The reaction proceeded to 67 percent conversion of starting material; however, a small amount of toluene was also generated in the reaction, presumably from the
formation of tolyl radicals in the presence of Ni(I) intermediates. Nakamura also observed buildup of toluene in reactions that involve bromotoluene derivatives. Reaction of \( m \)-bromotoluene (2b) with hexylmagnesium bromide proceeded to 85 percent conversion. The largest KIE value of 1.007 is observed at carbon #3. Values of 1.003 and 1.004 are also observed within the ring. Because carbon #3 demonstrates a much higher value than all others, the C-Br bond cleavage step is the dominant pathway at the FIS. Taking this into account with the above data, we conclude that the FIS is dependent not only on halide type, but also the position of the methyl substituent. Chlorides have a higher energy barrier for oxidative addition relative to bromides, and we speculate this to be the reason for the observation of \( \pi \)-complexation for all chloride derivatives. The steric effect of the methyl substituent on \( o \)-bromotoluene (1a) is believed to be the reason for the observation of \( \pi \)-complexation, since \( m \)-bromotoluene and \( p \)-bromotoluene exhibit KIE values characteristic of the C-Br bond cleavage step. Kochi also observed a steric effect in the rate of oxidative addition of Ni(PEt\(_3\))\(_4\) with aryl halides, where bromobenzene as the substrate exhibited a rate approximately four times faster than the methylsubstituted aryl halides.\(^4\) Interestingly, incorporation of more than one methyl substituent on the ring did not change the rate relative to one methyl substituent.
Figure 4.4. Experimental KIE values of 2-bromo-3-methylthiophene, 2-bromo-5-methylthiophene, and 2-bromo-5-propylthiophene substrates. Similar to the bromotoluene derivatives, the FIS is dependent on substituent position. For all integral values and standard deviations of measurements, see tables 4.1 to 4.3 in the experimental section.

Observation of Ni(0) interactions with thiophene derivatives was also observed to behave in a similar trend to the bromotoluene derivatives. Molecule 3a (Figure 4.4) exhibits enrichment in $^{13}$C at positions #4 and #5 to yield KIE values of 1.024 and 1.014, respectively. This result implies that π-complexation is the FIS during the OA process and strongly suggests that the π-system does indeed play a dominant role, however, any participation of the sulfur lone pairs cannot be discounted. The observation of zero enrichment at carbons #2 and #3 is again due to the steric effect constructed by the methyl substituent at the 3-position. The reaction proceeded cleanly to 98 percent conversion with no byproducts other than the initial bithiophene formation to generate the active Ni(0).

Relocation of the substituent to the 5-position (3b in Figure 4.4) indeed changes the FIS characteristic of C-Br bond cleavage, giving a $^{13}$C enhancement exclusively at the 2-position to yield a KIE value of 1.007. The carbons in positions 3, 4, and 5 yield a KIE of ~1, signifying a negligible role at the FIS. In addition to target product, the reaction also yielded 5',5-dimethyl-2',2-bithiophene and 2',2'-bithiophene, with an overall 80% conversion of 3b. The absence of an ortho-
substituent allows oxidative addition to occur directly without the need for prior π-complexation. Extension of the alkyl chain (3c in Figure 4.4) had no effect. The FIS remained the same as observed by sole enrichment in the 2-position yielding a KIE of 1.012. KIE values of 1.002 for carbons #3 and #5, as well as 1.005 for carbon #4, are much smaller than the observed value of 1.012 at the 2-position. The bromothiophene derivatives (3a-c) essentially follow the same trend as the bromotoluene derivatives (2a-c).

In a previous report, the yield of Ni(0) oxidative addition with surface bound haloarenes was investigated.\textsuperscript{10} It was found that thienyl halides without an ortho substituent exhibited superior oxidative addition yields compared to thienyl halides with an ortho substituent. The demonstrated KIE results rationalize these previous results.

\begin{figure}[h]
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\includegraphics[width=\textwidth]{figure4_5.png}
\caption{Scheme demonstrating the approach of Ni(0) to a thienyl bromide interface. The presence of an ortho substituent substantially increases the sterics of the OA reaction, as confirmed by KIE values of 3a-c.}
\end{figure}
In surface-confined systems, the two-dimensional nature of the interface limits the ability of Ni(0) to π-complex with the immobilized aryl halides. When molecules based on 3a are tethered to a surface via the 5-position, carbons #4 and #5 are likely to be submerged within the monolayer (Figure 4.5). Furthermore, there is an additional aliphatic chain at the 5-position that is used for surface tethering, providing an additional steric effect on the π-system. On the other hand, when there is no substituent in the ortho position, the Ni(0) catalyst can directly undergo the C-Br bond cleavage step, as shown by the KIE values for molecules 3a-c (Figure 4.4).

Also noteworthy are the relative distribution of products. In all reactions with thiophene derivatives where the substituent is not ortho to the halide, homocoupled product is observed (~10%). In all cases where an ortho substituent is present, only the target product is obtained. This agrees well with previous findings at surfaces.

Interestingly, some cross coupling reactions did not proceed under the reaction conditions used in this report. The coupling of 2-chloro-3-methylthiophene or 2-chloro-5-propylthiophene with 2-thienylmagnesium chloride proceeded to less than 5% conversion. To elucidate whether surface-bound unsubstituted aryl chlorides followed suit, a ferrocene capping agent was used to quench surface-tethered (thienyl)Ni(II)-Cl species generated by the oxidative addition of Ni(0). This coupling reaction generates a surface bound redox couple, which can be directly probed using cyclic voltammetry. The observed (aryl)Ni(II)-Cl initiator coverage values were on the order of 6×10^{12}/cm², giving an overall OA yield of 3%, which is approximately several times lower than initiator values obtained using unsubstituted thienyl bromides.

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In addition, attempts to couple 2-thienylmagnesium chloride with o-bromotoluene also did not proceed. In this situation, we hypothesize that the stable π-complex between Ni(0) and bithiophene generated in situ prevents the Ni(0) from complexing with o-bromotoluene. In KCTP, this preferential complexation phenomenon is observed in the synthesis of poly(3-hexylthiophene)-b-poly(p-hexyloxyphenylene). The block copolymer can only be synthesized through polymerization of the phenylene block first and not the other way around. The authors attribute this observation to the higher affinity for Ni(0) π-complexation with the thiophene block.

**Conclusion**

Kumada coupling reactions were carried out with an array of haloarenes, and the resulting kinetic isotope effect (KIE) values were calculated based on the experimental NMR integrations of starting materials before and after the Kumada coupling reaction. Cr(acac)$_3$ was used as a relaxation agent to decrease the $T_1$ values of the molecules under study, which significantly decreased the overall NMR time. Based on the data obtained, it was proposed that the first irreversible step in the oxidative addition of Ni(0) with haloarenes is not always π-complexation, but rather the bond cleavage step itself. Furthermore, the FIS is dependent on factors such as substituent position and halide type. Due to the increased energy barrier toward oxidative addition to chloroarenes, the FIS was found to be OA regardless of the position of the methyl substituent. In the case of bromotoluene derivatives, the FIS is OA when the substituent is located *para* or *meta* to the bromide. When the substituent is *ortho* to the bromide, π-complexation is observed at the FIS. The
oxidative addition of Ni(0) catalysts to haloarenes is also very sensitive to the steric properties of the substrate, regardless of halide type as shown by the negligible KIE values of carbons within the ring nearest to the substituent. This is the reason for the observation of $\pi$-complexation instead of C-Br bond cleavage for the o-bromotoluene substrate (2a). These results provide further insight toward the mechanism of oxidative addition of Ni(0) with aryl halides.

The Kumada coupling reaction is widely being adopted for numerous applications, especially in the rapidly growing field of conjugated polymer synthesis from external initiators immobilized to surfaces. Facile oxidative addition of Ni(0) must occur to generate (aryl)Ni(II)-X species at the interface. Based on the results in this work, it is suggested that surface immobilized aryl halides must not have a substituent ortho the aryl halogen bond to facilitate oxidative addition at the interface. Overall, this report has provided a more in depth understanding of Ni(0) interactions with haloarenes. Future studies will be centered among analysis of different substrate structures with varying electronic properties, as well as the use of palladium catalysts.
References


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CHAPTER 5
CONCLUSION AND OUTLOOK

Conclusion

In this work, conjugated polymers have been fabricated from a variety of substrates using Surface-Initiated Kumada Catalyst-Transfer Polycondensation (SI-KCTP). This grafting from route yields a high density of conjugated polymer chains with respectable film thickness values ranging from ten to 65 nm. Film thickness values of surface-bound polymer chains fabricated through a grafting to methodology are severely limited due to polymer chains being in their entropically favored coiled state, yielding a “mushroom-like” geometry at the interface. This causes nearby reactive sites for surface immobilization of additional polymer chains to be kinetically blocked, and as a result the number of polymer chains per area on the surface is low. Using a grafting from methodology, the number of polymer chains that can be immobilized is limited only by the density of small molecule polymerization initiators at the surface. For this reason, very high grafting densities can be achieved relative to grafting to, giving rise to a brush-like architecture. A major portion of this work is dedicated to the understanding and development of a rational design protocol for generating surface-bound initiators for SI-KCTP. This has significant importance, as the initiator density plays an important factor in the final density of polymer chains after polymerization. As a result of the studies in this
work, very uniform and robust conjugated polymer thin films are fabricated and analyzed using a variety of analytical techniques.

Chapter two of this dissertation represents the first report of a surface-bound conjugated polymer fabricated in a grafting from approach on conducting substrates using SI-KCTP. A major factor that allows for the successful grafting of the films is the nature of catalyst species used. The use of a very reactive Ni(0) species in the generation of the surface-bound polymerization initiator was critical for successful grafting of poly(thiophene) and poly(phenylene). This initial report was centered on the use of two monodentate phosphine ligands coordinated to the nickel catalyst on the initiator structure, which is not optimal for KCTP. The generation of high performance bidentate phosphine ligands is necessary to add further control to the polymerization; however, the generation of such a surface-bound structure is not trivial. In addition, elimination of bulky solubilizing chains on the monomer structure was also necessary for successful grafting, demonstrating the steric sensitivity of the SI-KCTP technique. This report was highlighted as “The Skyscraper Approach to Nanoelectronics” in Chemical Science.

Chapter three is centered on the generation and characterization of bidentate phosphine ligated SI-KCTP initiators for high performance polymerization. An innovative method of characterizing the density and homogeneity of surface-immobilized KCTP initiators was developed, and revealed for the first time the nature of the nickel-functionalized interface. It was found that extensive side reactions are occurring between initiator sites adjacent to one another, thus limiting the overall grafting density. In addition, the extent of side reactions was dependent
on the bite angle of the phosphine ligand used on the initiator structure. Although the grafting density was limited to less than 20 percent of a monolayer, uniform poly(3-methylthiophene) films were fabricated up to a thickness of 65 nm. This is a significant improvement over earlier results reported in chapter two.

Chapter four offers additional insight into Ni(0) interactions with haloarenes during the oxidative addition step prior to the coupling of Grignard type nucleophiles. This oxidative addition reaction has been debated in the literature regarding its mechanism, and has been heavily utilized to generate SI-KCTP initiators on a variety of substrates in previous chapters of this dissertation. It was found that the first irreversible step (FIS) of the oxidative addition process is highly dependent on the type of halide (bromine or chlorine) and the position of the alkyl substituent on the ring. This chapter has provided a detailed understanding of the Kumada cross-coupling reaction with a diverse array of aryl halides.

**Future Work**

The work in this dissertation has provided a successful route toward the grafting of conjugated polymers. The Kumada Catalyst-Transfer Polycondensation (KCTP) technique is a very new methodology that has only been developed within the last decade. A number of adaptations to the technique were necessary to allow for successful grafting of conjugated polymers directly from a variety of surfaces (SI-KCTP). The thin films created in this work are currently being used in photovoltaic devices as an interfacial layer on ITO. This will allow for more efficient hole collection at the anode, thus increasing overall device efficiency. Furthermore, the scope of the KCTP technique can be increased through the use of monomers that
yield low bandgap conjugated polymers. In addition to the photovoltaic arena, the films will also find applications in the study of electron transfer reactions through conjugated materials, where the conjugated polymer is used to tether redox active molecules directly to electrodes.

Adaptation of the SI-KCTP technique to work with a variety of electron rich and electron deficient monomers may require the use of palladium catalysts. However, palladium catalysts are difficult to immobilize on the surface due to their decreased reactivity toward oxidative addition. For this reason, immobilization of palladium will require higher temperatures and this can be problematic on gold substrates that utilize thiol-based chemistry. Chapter 3 of this dissertation provides a powerful technique for characterizing surface-bound organometallic species, and will enable one to optimize procedures for the generation of surface-bound palladium initiators.

Final Remarks

The SI-KCTP technique offers a lot of potential in the creation of unique electroactive films for electronic devices. Compared to spin-coated conjugated polymer films, surface-initiated polymerization offer other advantages such as the ability to prepare uniform coatings on objects of any shape, ability to control grafting density based on initiator surface coverage, and simplified polymer separation. Furthermore, the covalent immobilization of conjugated polymers to conductive substrates not only prevents delamination, but also offers greater versatility toward spin coating an additional layer if both layers are soluble in the same solvent.
APPENDIX A

$^1$H NMR SPECTRA OF COMPOUNDS

Figure A-1: $^1$H NMR spectrum of ferrocen-2-yl(5-bromothiophen-2-yl)methanone.
Figure A-2: $^1$H NMR spectrum of 2-ferroceny1-5-bromothiophene.

Figure A-3: $^1$H NMR spectrum of 8-(5-bromothiophene-2-yl)octane-1-thiol.
Figure A-4: $^1$H NMR spectrum of 8-(5-bromo-3-methyl-thiophene-2-yl)octane-1-thiol.

Figure A-5: $^1$H NMR spectrum of 2-bromo-3-methyl-5-iodothiophene.
Figure A-6: $^1$H NMR spectrum of (6-(5-bromothiophen-2-yl)hexyl)phosphonic acid.

Figure A-7: $^1$H NMR spectrum of (3-((5-bromo-4-methylthiophen-2-yl)propyl)trichlorosilane.
Figure A-8: $^1$H NMR spectrum of (4-bromobenzyl)phosphonic acid.