Development of Transition Metal-Catalyzed Polymerization Reactions and their Applications for the Preparation of Well-Defined Conjugated Polymer Architectures

Carlos Anthony Chavez

Louisiana State University and Agricultural and Mechanical College

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DEVELOPMENT OF TRANSITION METAL-CATALYZED POLYMERIZATION REACTIONS AND THEIR APPLICATIONS FOR THE PREPARATION OF WELL-DEFINED CONJUGATED POLYMER ARCHITECTURES

A Dissertation

Submitted to the Graduate Faculty of the Louisiana State University and Agricultural and Mechanical College in partial fulfillment of the requirements for the degree of Doctor of Philosophy

in

The Department of Chemistry

by

Carlos Anthony Chavez
B.S., University of New Mexico, 2010
December 2015
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<th>Full Form</th>
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<tbody>
<tr>
<td>acac</td>
<td>Acetylacetonate</td>
</tr>
<tr>
<td>ATRP</td>
<td>Atom-Transfer Radical Polymerization</td>
</tr>
<tr>
<td>bipy</td>
<td>2,2'-bipyridyl</td>
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<td>HOMO</td>
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<td>IPr</td>
<td>1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene</td>
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<td>KCTP</td>
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<td>NIR</td>
<td>Near-infrared</td>
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<tr>
<td>NMR</td>
<td>Nuclear Magnetic Resonance</td>
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<tr>
<td>NP</td>
<td>Nanoparticle</td>
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<tr>
<td>OLED</td>
<td>Organic Light-emitting Diode</td>
</tr>
<tr>
<td>P3AT</td>
<td>Poly(3-alkylthiophene)</td>
</tr>
<tr>
<td>P3HT</td>
<td>Poly(3-hexylthiophene)</td>
</tr>
<tr>
<td>P3OT</td>
<td>Poly(3-octylthiophene)</td>
</tr>
<tr>
<td>PBTz</td>
<td>Polybenzotriazole</td>
</tr>
<tr>
<td>PCBM</td>
<td>Phenyl-C61-butyric acid methyl ester</td>
</tr>
<tr>
<td>PDCI</td>
<td>Perylenedicarboximide</td>
</tr>
<tr>
<td>PDI</td>
<td>Polydispersity Index</td>
</tr>
<tr>
<td>PEDOT</td>
<td>Poly(3,4-ethylenedioxythiophene)</td>
</tr>
<tr>
<td>Pdot</td>
<td>Polymer Dot</td>
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<tr>
<td>Abbreviation</td>
<td>Full Form</td>
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<td>--------------</td>
<td>-----------------------------------------------</td>
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<tr>
<td>PF</td>
<td>Polyfluorene</td>
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<tr>
<td>Ph</td>
<td>Phenyl</td>
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<tr>
<td>PNIPAm</td>
<td>Poly-(N-isopropylacrylamide)</td>
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<tr>
<td>PPE</td>
<td>Poly(p-phenylene ethynylene)</td>
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<tr>
<td>PPEV</td>
<td>Poly(p-phenylene ethynylene vinylene)</td>
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<tr>
<td>ppm</td>
<td>Parts-per-million</td>
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<tr>
<td>PPP</td>
<td>Poly(p-phenylene)</td>
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<tr>
<td>PPV</td>
<td>Poly(p-phenylene vinylene)</td>
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<tr>
<td>PS</td>
<td>Polystyrene</td>
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<td>PT</td>
<td>Polythiophene</td>
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<td>Polyvinyl chloride</td>
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<td>Quantum Dot</td>
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<tr>
<td>rr</td>
<td>Regioregular</td>
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<tr>
<td>Ruphos</td>
<td>2-dicyclohexylphosphino-2',6'-diisoproxybiphenyl</td>
</tr>
<tr>
<td>SANS</td>
<td>Small-angle Neutron Scattering</td>
</tr>
<tr>
<td>TBAF</td>
<td>Tetrabutylammonium fluoride (Bu₄NF)</td>
</tr>
<tr>
<td>TDMPP</td>
<td>Tris(2,6-dimethoxyphenyl)phosphine</td>
</tr>
<tr>
<td>TEM</td>
<td>Transmission Electron Microscopy</td>
</tr>
<tr>
<td>TEMPO</td>
<td>2,2,6,6-tetramethylpiperidine-1-oxyl</td>
</tr>
<tr>
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<td>Thermogravimetric Analysis</td>
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<tr>
<td>TBDMS</td>
<td>tert-Butyldimethylsilane</td>
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<td>UV-vis</td>
<td>Ultraviolet-visible</td>
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<td>XPS</td>
<td>X-ray Photoelectron Spectroscopy</td>
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ABSTRACT

The synthesis of conjugated polymers and design of complex materials based on them have become increasingly popular as the demand for low-cost efficient and processible optoelectronic and semiconducting devices escalates. While advanced applications of polymeric materials require some degree of sophistication, success can be achieved through careful consideration of polymerization techniques and methodologies. Controlling critical aspects of the polymerization process allows for synthesis of complex macromolecular architectures possessing unique and novel properties that may be worth of further comprehensive investigation.

This dissertation primarily focuses on the development and preparation of well-defined hierarchical macromolecular architectures. The foundation of this work encompasses the transition metal catalytic synthetic methods used to maintain a controlled chain-growth polymerization to yield conjugated polymers. These methods enabled design of a series of novel complex conjugated polymeric materials. A number of intriguing characteristics of these higher ordered polymeric systems are described, in addition to studies on how these characteristics, such as the control of exciton migration enabling modulation of energy transfer, lead to a greater understanding of the fundamental properties inherent of conjugated polymers.

While the preparation and synthesis determine the properties of conjugated polymers at the molecular level, supramolecular organization can have even bigger impact on the properties of materials. Investigations into supramolecular organization and structural studies of these organized architectures, while a difficult challenge, were carried out using small-angle neutron scattering and electron microscopy.
A last part of this dissertation explores the stereoselective preparation and properties of a novel class of conjugated polymers poly(p-phenylene ethynylene vinylene)s (PPEVs). These materials possess unique spectroscopic and physical properties, such as pronounced mechano-fluorescent behavior, which can be utilized in future optical and sensing devices.
CHAPTER 1. SYNTHESIS, CHARACTERISTICS, AND APPLICATIONS OF \( \pi \)-CONJUGATED MATERIALS: AN INTRODUCTION

1.1. Introduction to Conjugated Polymers

Conjugated polymers have significantly increased in popularity over the past three decades due to their unique optical and semiconducting properties, making them ideal candidates for many functional applications such as organic photovoltaic cells,\(^1\)-\(^2\) chemical sensory devices,\(^3\)-\(^4\) organic light emitting diodes (OLEDs),\(^5\) etc. The groundbreaking discovery of the semiconducting polymer polyacetylene made collectively by Shirakawa, MacDiarmid, and Heeger in 1977 brought new insight into materials used for electronic devices, as conjugated polymers are carbon-based molecules as opposed to inorganic semiconductors. What they found to be of interest was that thin-films of polyacetylene, when exposed to vapors of iodine, increased their ability to conduct electricity ranging from a low semiconductor to almost metal-like conducting properties.\(^6\) This would open the gates to many areas of science in order to explore the semiconducting properties of plastics.

Conjugated polymers are characterized by their extended \( \pi \)-conjugation throughout the length of the polymer chain by incorporation of only sp and/or sp\(^2\) hybrid carbon centers. Similarly they may also contain hybridized heteroatoms possessing lone electron pairs such as S, N, Se, etc. As most conjugated chromophores absorb in the UV-visible range, this would allow for their excitation energies to also lie within the visible range, making them excellent optoelectronic materials. The alternating pi-sigma-pi bond throughout a conjugated backbone both stabilizes the molecule and alters electronic properties of the increasingly delocalized molecule. By increasing the conjugation length, this decreases the HOMO and LUMO levels, bringing them closer to that of a metallic conductor where there is no distinct valence and conduction bands but a series of continuous energy levels. As these aromatic monomers extend from small molecule
to oligomers to polymers, their electronic band structure is successively distributed, decreasing the overall HOMO–LUMO level.\textsuperscript{7} While conjugated polymers have never reached the level of metal conductors in which they have minimal impedance on conductivity, they do have the ability to resemble that of inorganic semiconductors. Polymers such as poly($p$-phenylene vinylene) (PPV), poly($p$-phenylene ethynylene) (PPE), poly($p$-phenylene) (PPP), and polythiophene (PT) have all been significantly explored and have made large contributions to materials and device fields (Figure 1.1).

![Chemical structures of various conjugated polymers](image)

**Figure 1.1.** Representative examples of conjugated polymers described throughout literature.

While there has been extensive research on the preparation of various classes of conjugated polymers, this dissertation will focus mainly on that of polythiophenes.

### 1.2. Processability of Regioregular Polythiophenes

Ideally, it would be beneficial for conjugated polymers to exist as unsubstituted delocalized PT molecules similar to that portrayed in Figure 1.1. This was typically done by electrochemical methods or oxidative chemical polymerization using stoichiometric oxidants (e.g. FeCl\textsubscript{3}).\textsuperscript{8} However, this was only successful in producing low molecular weight oligomers or polymers with little control over molecular structure. In order to increase the molecular weight of conjugated polymers, or prepare better-defined systems, they must contain solubilizing side-groups, such as long aliphatic hydrocarbons, in order to perform polymerization in homogenous
conditions without precipitating during sequential growth as well as post-polymerization processing. This led to numerous polymerization methods in which aromatic monomers can be covalently bound via homogenous cross-coupling polycondensation reactions using transition metal catalysts.\(^9\)

While previous chemical syntheses of these polymers also utilized transition metal catalysts, it was now important to consider the control of regioselectivity within poly(3-alkylthiophene) (P3AT). As a 3-alkylthiophene unit is not symmetrical, there exists three potential regioisomers to form upon coupling (Figure 1.2).

Figure 1.2. Regioisomers of poly(3-alkylthiophene) and the effects on the planarity.

A head-to-tail (2-5’) coupling is the preferred regioisomer as it does not cause any steric repulsion from neighboring alkyl chains resulting in a planar backbone due to the low energy conformation that exists. Alternatively, head-to-head (2-2’) and tail-to-tail (5-5’) couplings cause a twisting in the conjugated backbone of the polymer chain, resulting in loss of delocalization. The lack of conjugation within a polymer chain hinders the conducting properties of polythiophenes making them undesirable as electronic materials. Colloquially known as
regioregular (rr) P3ATs, these consist only of H-T couplings while P3ATs containing any occurrence of H-H or T-T couplings is known as regioirregular or regiorandom.

1.3. Step-growth vs Chain-Growth Polymerizations toward Poly(3-alkylthiophene)

The most common means of synthesizing a myriad of different classes of conjugated polymers is that of a traditional Pd cross-coupling polycondensation. Stille and Suzuki polymerizations have all produced high molecular weight P3ATs yet they suffer from very low regioselectivity (Figure 1.3).

This is mainly due to the fact that these polymerizations are occurring via a step-growth mechanism rather than through a chain-growth process.

![Figure 1.3. Preparation of poly(3-alkylthiophene) by step-growth polymerization.](image)

*Step-growth polymerization* is defined as occurring in a step-wise process where a reaction between functional moieties is taking place. In this case, different sized growing species can react with each other at any given time (e.g. dimer bonds to hexamer, tetramer bonds to monomer, trimer bonds to heptamer, etc.). However, one major disadvantage of step-growth polymerizations is high polydispersity of the resulting polymer, meaning that the molecular weight of polymer chains vary greatly (i.e. $M_w/M_n >> 1.0$). Contrary to the step-growth method is *chain-growth polymerization* where this is defined as having many individual growing chains in tandem (i.e. only a monomer can react with a growing polymer chain). Chain-growth polymerization requires a reactive initiator to begin the growing process while step-growth polymerization does not. This reactive species can be either a cation, anion, radical, etc. that
upon reacting with the monomer, initiates the propagating chain by forming a new reactive center at the end of the polymer chain that can continually react with another monomer. This would result in polymers with narrow molecular weight distributions (low polydispersity), meaning all the chains are roughly the same molecular weight (i.e. $M_w/M_n \sim 1.0$).

One type of chain-growth polymerization where no “chain-breaking” reactions can occur is termed a *living polymerization*. In this type of polymerization, “chain-breaking” reactions such as chain-transfer or termination do not occur resulting in a dormant reactive species at the end of a growing polymer chain once all monomer is consumed. This concept is very important for functional polymers as it gives a greater ability to control every aspect of the polymerization. Theoretically there is only one initiator per polymer chain meaning that the end group is functionalized with the initiator. If we look at the other end of the polymer chain, this would result in a dormant reactive species, which can be either 1) terminated or 2) allowed to continue growth with the addition of monomer. Living polymerization allows for both end-group functionalization as well as control of well-defined block copolymers or other macromolecular structures. Additionally, as this is still defined as a chain-growth process without chain-transfer or termination, all of the resulting polymer chains would theoretically be the same molecular weight. As we will see, the preparation of polythiophenes using a “quasi-living” chain-growth mechanism has made great strides to developing useful conjugated materials.

1.4. Developments in Controlled Chain-Growth Polymerizations toward Conjugated Polymers

1.4.1. In-situ Generated Catalytic Initiator for Kumada-catalyst Transfer Polymerizations.

As stated previously, polythiophenes could be prepared via various step-growth polymerization methods as well as oxidative chemical processes resulting in high polydispersity regiorandom polymers. However, development of Kumada catalyst-transfer polycondensation
(KCTP) (also called the Grignard metathesis method or GRIM) of thienylmagnesium monomers with a Ni(II) catalyst by McCullough\textsuperscript{13} and Yokozawa\textsuperscript{14} opened up new venue for the preparation of not only regioregular P3ATs, but other electron-rich conjugated polymers. Arylmagnesium monomers are easily prepared by the addition of 1 eq. of Mg (typically organomagnesium compound such as \textit{i}-PrMgCl) to an aromatic dihalogen monomer. Subsequent addition of a catalytic amount of a dihalogenated Ni(II) coordinated to an electron-rich bidentate phosphine ligand (usually Ni(dppp)Cl\textsubscript{2}, where dppp = 1,3-bis(diphenylphosphino)propane) to a solution of arylmagnesium monomer initiates the polymerization very rapidly. This Kumada cross-coupling cycling can be summed up in Figure 1.4 where the initial rate-determining step is classified as transmetalation, followed by reductive elimination and the continuing catalytic cycle consisting of i) oxidative addition, ii) transmetalation, iii) reductive elimination steps until the reactive species is quenched or the monomer is consumed completely.\textsuperscript{15} Another important step to note is the catalyst transfer step in which the strong π-coordination prevents dissociation of the catalyst. It has been shown by McNeil \textit{et al.} that the electron-donating ability of the associated π-complexed ligand is what controls the chain-growth character of the polymerization as it increases stability of the walking catalyst.\textsuperscript{16} Kiriy \textit{et al.} has also shed some light on this process where they have determined that the π-coordinated walking catalyst is actually in a “random-walk” where it can move in both directions along the propagating chain.\textsuperscript{17} McCullough and Yokozawa determined that this was, in fact, occurring via a “quasi-living” chain-growth mechanism as they could both 1) control the degree of polymerization through amount of catalyst loading and 2) increase the degree of polymerization through the addition of excess monomer.\textsuperscript{15} While the Kumada-catalyst transfer polymerization (KCTP) was groundbreaking in producing highly regioregular and low
polydisperse P3ATs through a quasi-living mechanism, there is a clear disadvantage when looking at the mechanistic pathway.

As was stated above, the rate-determining step is controlled by the in situ generated initiating species after transmetalation of two monomers since the Ni(dppp)Cl$_2$ is acting as both the initiator and catalyst. After reductive elimination of the two thienyl monomers, we end up with what has been termed as an “associated pair.” This associated-pair will always result in a T-T coupling, lacking 100% of its potential regioregularity. Furthermore, by generating the initiating species in situ the polymerization would suffer from increased polydispersities due to the

Figure 1.4. Mechanism of Kumada chain-growth living polymerization towards P3ATs. Reproduced with permission from Ref. 15. Copyright © 2008 American Chemical Society.
relatively slow reactivity of the initiating species. Ideally, initiation should occur all at the same time in order to create equilibrium between the propagating catalyst and dormant species.

1.4.2. Ex-situ Generated Catalytic Initiators for Kumada-catalyst Transfer Polymerizations.

In order to increase the reactivity and ability to tailor polymer chains in a controlled manner, the concept of ex situ generated catalytic initiators were first demonstrated by Kiriy\textsuperscript{18} and Luscombe.\textsuperscript{19} Ex situ generated initiators (or external initiators) are preformed Ni(II) catalytic complexes obtained by the reaction of a Ni(0) complex with an aryl halide via oxidative addition similar to the oxidative addition in a Yamamoto cross-coupling reaction (Figure 1.5).

Figure 1.5. Generation of ex situ catalytic initiators for KCTP.

While commonly available Ni(PPh\textsubscript{3})\textsubscript{4} could be used to initiate polymerization after oxidative addition with an aryl halide, it results in low molecular weight oligomers and high polydispersity ($M_\text{w}/M_\text{n}$ ~2.0). In order to prevent undesired disproportionation\textsuperscript{20} (Figure 1.6) during polymerization or Yamamoto aryl-aryl coupling caused by monodentate ligands, ligand exchange with a bidentate phosphine ligand could be accomplished after oxidative addition to form a square-planar complex where the phosphines are cis rather than trans to each other. The increased stability from bidentate chelating ligands improves the efficiency of the KCTP by minimizing disproportionation and chain-transfer events yet allows for a random-walking of the Ni catalyst to traverse the length of a monomer through formation of a Ni(0) $\pi$-complex.
Although the key role of Ni(0) \( \pi \)-complex has been postulated in many mechanistic discussions, it has not been actually observed, and therefore it was often referred to as “associated pair”.

Figure 1.6. Simplified mechanism of disproportionation that can occur during KCTP with monodentate ligand.

However, recently McNeil observed more substantial evidence in favor of the \( \pi \)-complex, which now makes more solid ground for its actual role in polymerization.\(^{16}\) Reported molecular weights in the method of externally-initiated KCTP are very high with moderate polydispersities and regioregularity. However, the use of monodentate ligand PPh\(_3\) in the first step of catalyst generation limits the control of the KCTP as it typically remains throughout the reaction mixture even after ligand exchange. Additionally, due to the reactivity of these external initiators it makes them highly sensitive to oxygen and moisture, making it very hard to purify. Without proper purification, monodentate ligand is almost impossible to entirely remove even with a careful purification protocol.

Furthermore, external initiation acts as both a highly reactive catalyst but more importantly an initiator. This initiating species allows for the ability to functionalize terminal ends accordingly, whether that is at the onset of the growing chain or the terminus upon quenching. Complete control of molecular structure makes the concept of external initiation very appealing for synthesis of complex macromolecular architectures, which will be discussed in chapters 2, 3, and 4.
1.4.3. Pd-catalyzed, Suzuki-Miyaura and Stille-Controlled Catalyst Transfer Polymerization.

External initiation using an aryl-Pd complex also leads to a chain-transfer polycondensation polymerization similar to that of the KCTP mechanism but instead requires boronic ester functionalized monomers. Traditionally Suzuki-Miyaura step-growth polymerizations (Figure 1.3) act upon two different bifunctional monomers in one pot: diboronic ester monomer and aryl dihalide resulting in very large polydispersities with little to no control over the polymerization. However, Yokozawa recently demonstrated that when functionalizing a single monomer with a boronic acid and halide functionalization on opposing ends, the resulting polymerization seems to occur via catalyst transfer mechanism with high molecular weights and low polydispersities. The use of *ex-situ* generated $t$-Bu$_3$PPd(Ph)Br as the catalyst allowed for the investigation into the catalyst transfer mechanism since the aryl group on the initiating species would be incorporated as an end-group of the growing polymer chain.

![Figure 1.7](image)

**Figure 1.7.** Controlled chain-growth polymerization of P3HT using Suzuki-Miyaura cross-coupling.

Huck and coworkers went on to explore various Pd-catalysts in order to perform Suzuki-Miyaura chain-growth polymerization towards conjugated polymers. The reaction of Pd($t$-Bu$_3$P)$_2$ with a corresponding aryl halide resulted in numerous polyaromatic initiators that could be used to obtain well-defined conjugated polymers. It was also shown by Hu that Pd$_2$(dba)$_3$ (dba = dibenzalacetone) and phosphine ligand $t$-Bu$_3$P react with an aryl iodide, however aryl bromides showed little control over initiation resulting in high polydispersities.
While boronic ester/halide functionalized monomers result in chain-growth preparation of various conjugated polymers using a Suzuki-Miyaura cross-coupling method, stannyl/halide monomers can be used similarly for polymerization by Stille cross-coupling. Bielawski recently demonstrated the synthesis of poly(p-phenylene ethynylene) (PPE) by chain-growth catalyst transfer polymerization with the use of $t$-Bu$_3$PPd(Ph)Br catalyst along with various phosphine ligands and CuI.$^{24}$ This method demonstrated the ability to grow well-defined block copolymers as well as surface-initiated chain-growth on the surface of silica nanoparticles.

Figure 1.8. Stille chain-growth polymerization towards PPE.

1.4.4. N-Heterocyclic Carbene Ligands Stabilizing the Catalyst Transfer.

Due to the electron-rich nature of N-heterocyclic carbenes (NHCs), various groups sought to utilize their strong σ donation in order to facilitate the catalyst-transfer step. McNeil has previously reported on the electronic stabilization of the Ni(0) π-complex being mainly attributed to the electron donating ability of the phosphine ligands in traditional Ni(dppe)$_2$ (where dppe = bis(diphenylphosphinoethane)) KCTP as determined through multiple polymerization experiments with variable phosphine ligands.$^{25}$ This led to the use of an NHC-ligated Pd catalyst in order to polymerize various conjugated monomers by KCTP.$^{26}$ While the 2,6-diisopropylphenyl substituents on the NHC
provided steric bulk, the electron-donating ability of the NHC itself could provide the stabilization energy needed to increase the rate of catalyst transfer. While P3HT and PPP could be synthesized in a controlled chain-growth fashion it should be noted that polyfluorene (PF) could not be obtained by this mechanism. MALDI-TOF end-group analysis showed that there was in fact some amount of chain-growth and chain-termination that was occurring at low molecular weights. The use of NHC-ligated Pd catalyst also led to low regioregularity of P3HT as the authors suggested that the major regioisomer would be consumed first, followed by the slow reactivity of the minor regioisomer.

A similar NHC-ligated Ni catalyst could also be used for the chain-growth preparation of P3HTs as was described by Mori. While it acts similarly to the described Pd analog, in this case Mori was using 2-chloro-2-alkylthiophenes in order to generate a thiencwmagnesium monomer from a stoichiometric amount of magnesium amide TMPMgCl • 3 LiCl (chloromagnesium 2,2,6,6-tetramethylpiperidide lithium chloride salt), or with the use of a Grignard reagent and catalytic amount of a secondary amine (Figure 1.9).

![Figure 1.9. 2-chloro-3-hexylthiophene polymerization to form P3HT using NHC-ligated Ni catalyst.](image)

It is interesting to note that while Ni(dppp)Cl2 did not act as a catalyst in this case, the NHC-ligated Ni catalyst proceeded to form P3HT in a chain-growth fashion with relatively low polydispersity and high degree of control in regards to molecular weight. This is important, as
the polymerizations of Cl-substituted monomers are less commonly used than that of their Br- or I-substituted counterparts – a feature that can be useful in future explorations of various aromatic monomers.

Recently, Geng has described the synthesis of regioregular P3HT (rrP3HT) using an unusual Ni(IPr)(acac)₂ catalyst. The rrP3HTs were synthesized over a large number of catalyst loadings, demonstrating that the polymerization was occurring via KCTP. Regioregularity was reported to be upwards of 100% while maintaining low polydispersities. The efficiency of the polymerization was analyzed by DFT calculations that determined the increase of π-complex stabilization energy relative to traditional phosphine ligands.


Electron-rich (or p-type) monomers have been thoroughly investigated as they show relative ease of transition metal catalyst transfer compared to that of electron-deficient (or n-type) monomers. This can primarily be attributed to the weak association that the propagating nickel catalyst has onto the growing electron-deficient chain. This ultimately causes dissociation of the catalyst leading to a lack of control during polymerization, low molecular weights, and high molecular weight distributions. However, Seferos recently described well-defined chain-growth of electron-deficient polymers by increasing the electron-density on the Ni catalyst by means of an electron-donating diimine ligand (Figure 1.10). A series of diimine ligands were investigated ranging from electron-withdrawing to electron-donating, which according to DFT calculations showed that the ligand with an increased stabilization energy would be superior in chain-growth controlled polymerization. The electron-donating ligand bearing –OMe
substituents was in fact the superior ligand resulting in high molecular weight and low polydispersity polybenzotriazole (PBTz).

Figure 1.10. Synthesis of electron-deficient PBTz using diimine coordinated Ni(II) catalyst.

One variation to polymerizing electron-deficient monomers with the use of a naphthalenediimide radical anion active monomer was recently shown by Senkovskyy and Kiriy. When the active electron-deficient radical cation is treated with a Ni(II) catalyst, it allows for the strong π-coordination during the catalyst transfer step. It should be noted that the polymerization mechanism does not act as a KCTP since there was no evidence of polymerization after treatment of the monomer with a Grignard reagent, but more likely follows a mechanism of reductive coupling. Electron paramagnetic resonance (EPR) spectroscopy confirmed that there was in fact a radical anion being formed after treatment of naphthalenediimide with a reactive Zn via a single-electron transfer (Figure 1.11). After polymerization of the radical anion monomer was accomplished with Ni(dppe)Br$_2$ or PhNi(dppe)Br catalysts, characterization of the resulting polymers revealed that the polymerization was proceeding in a chain-growth fashion as apparent by the controlled molecular weight, low polydispersity, and incorporation of end-group when using an external initiator.
Huck and Kiriy also demonstrated the ability to synthesize alternating donor–acceptor polymers, which, as will be discussed in the next section, are extremely important for the fabrication of organic photovoltaics due to their decreased HOMO–LUMO gap and increased absorption area.\(^\text{32}\) The polymerization of D–A copolymers was accomplished using an ArPd(t-Bu\(_3\)P)Br catalyst in the presence of a base (CsF) and a crown ether under Suzuki-Miyaura cross-coupling conditions. The incorporation of the aryl group by MALDI-TOF as well as significant degree of molecular weight control and narrow molecular weight distribution again confirms the chain-growth mechanism.

1.4.6. Miscellaneous Chain-growth Polymerizations toward Conjugated Polymers.

Various other methods have been developed in order to prepare conjugated polymers via a controlled chain-growth process. One important method that undergoes chain-growth yet does not undergo catalyst transfer was demonstrated by Koeckelberghs et al. in which they prepared regioregular P3HTs via a zincated monomer with Pd(0) coordinated to Buchwald ligand Ruphos.\(^\text{33}\) While the approach is somewhat similar to a Negishi polymerization previously demonstrated by McCullough\(^\text{34}\) and Rieke,\(^\text{35-36}\) it was shown that the catalyst dissociates from the
growing chain, yet the chain-growth was controlled by the deactivation of the C–Br bond for oxidative addition by the electron-donation from the organozinc. So while the Pd(0)[Ruphos] dissociated from the growing chain, it can consequently undergo oxidative reinsertion at the terminal end of the P3HT chain. Similarly, Kiriy was able to synthesize polyfluorenes by extremely efficient Negishi chain-growth polymerization instead using a 1:1 mixture of Pd(CH$_3$CN)$_2$Cl$_2$ and ligand t-Bu$_3$P. While the polymerization was extremely fast with high turnover (even at ppm concentrations of the catalyst), it suffered from broad molecular weight distribution.$^{37}$ In another study, Koeckelberghs et al. also demonstrated a very efficient Negishi chain-growth polymerization of thieno[3,2-b]thiophene using PhPd(t-Bu$_3$P)Br, but it too suffered from a lack of catalyst transfer.$^{38}$

Yokozawa has sought after a catalyst transfer chain-growth polymerization to form poly($p$-phenylene vinylene) (PPV) as it is a very important optoelectronic material. He demonstrated that PPV with high molecular weight could be prepared either using a Suzuki-Miyaura or Mizoroki-Heck cross-coupling of AB-type monomers.$^{39-41}$ Suzuki-Miyaura process produced moderate molecular weight polymers but broad molecular weight distribution while the Mizoroki-Heck resulted in relatively high molecular weight polymers yet was found to proceed via a traditional step-growth polymerization due to predominance of chain-transfer events.

Another important polymerization technique developed by Ozawa et al. still involves the use of a transition metal catalyst yet does not require the use of conventionally employed reactive organometallic monomers. They demonstrated that formation of regioregular P3HTs via a dehydrohalogenative coupling (also known as direct arylation)$^{42}$ 2-bromo-3-hexylthiophene could be directly polymerized using Hermann’s catalyst and tris(2-dimethylaminophenyl)phosphine at high temperature (~125 ºC). Hermann’s catalyst and ligand
form a catalyst precursor which proceeds to produce high molecular weight polymer in relatively narrow molecular weight distributions at almost quantitative yield (~99% yield). While this is an attractive system for the synthesis of rrP3HTs, it suffers from formation of coupled polymer chains upon complete consumption of monomer resulting in molecular weights higher than expected (similar to disproportionation).

Recently, Swager et al. have developed a method of chain-growth polymerization leading to poly(ProDOT) (poly(propylenedioxythiophene)) by a Lewis-acid (SnCl$_4$) catalyzed chain growth of a 2-chloroalkylenedioxythiophene.$^{43}$

![Preparation of Poly(ProDOT) through Lewis-acid catalyzed controlled chain-growth polymerization.](image)

Figure 1.12. Preparation of Poly(ProDOT) through Lewis-acid catalyzed controlled chain-growth polymerization.

Again, this process does not occur via a catalyst transfer mechanism but follows a radical cation mechanism where a monomer of 2-chloroalkylenedioxythiophene reacts with the stannylated terminal end of the growing polymer chain, subsequently losing HCl as a by-product (Figure 1.12). While this method produces block copolymers and end-group functionalized polymers via
a chain-growth process, it requires high temperatures, which comes at a disadvantage when considering large-scale synthesis.

1.4.7. Transition Metal-free Chain-growth Polymerizations toward Conjugated Polymers.

Transition metals are difficult to remove from crude polymer mixtures, which can inhibit the conductive properties of semiconducting polymers. Moving towards transition metal-free controlled chain-growth preparation of conjugated polymers may be important for future synthetic developments as they would require little to no purification or undesired by-products. Sanji et al. have shown that chain-growth polymerization using a fluoride anion as a catalyst can proceed with using various trimethylsilane functionalized monomers (Figure 1.13).

\[
\begin{align*}
R &= \text{either trimethylsilylthiophene or trimethylsilylethynylbenzene.} \\
\text{Controlled anionic chain-growth occurs via } S_N Ar \text{ reaction of the bifunctional monomer. In the first step, a pentavalent silicon center is formed after treatment with } F^- \text{ rendering the carbon center nucleophilic. The nucleophilic carbon can then react quickly at the } para\text{-position on the perfluorararylbenzene. High molecular weights could be controlled by catalyst loading while still maintaining relatively low }
\end{align*}
\]

Figure 1.13. Transition-metal-free controlled polymerization using F$^{-}$ as a catalyst.
polydispersities. Furthermore, the polymer could be functionalized on the terminal end of the polymer chain, signifying the controlled chain-growth.

One process exemplified by the formation of PPP is through the chain-growth mechanism by nucleophilic radical substitution (S_{RN1}). Studer has developed a very elegant synthesis of alkyl-substituted poly(m-phenylene), poly(p-phenylene), or polynaphthalene using a stable radical initiator such as 2,2,6,6-tetramethylpiperidine N-oxyl radical (TEMPO) in the presence of a phenyl Grignard monomer identical to that of a KCTP monomer (Figure 1.14).

![Figure 1.14. Formation of PPP polymer via radical chain-growth polymerization of PPP using TEMPO.](image)

Initiation step occurs after homocoupling of two monomers to produce a biaryl radical anion. Subsequent loss of I⁻ starts a propagating radical initiator that cycles through i) radical anion generation, ii) loss of I⁻, and iii) formation of aryl radical species. However, molecular weights cannot be controlled by catalyst loading and molecular weight distributions are relatively broad meaning that this is unlikely to occur as a controlled catalyst-transfer process. Although it is not a controlled polymerization, it does give good insight into variable methods of synthesizing well-defined conjugated polymer materials.

### 1.5. Conjugated Polymers and Photoexcitation Energy Transfer

In order to produce functional devices from organic conjugated polymers, it is important to understand the mechanisms in which excitation energy is transferred within these systems. The
mechanism of energy transfer in conjugated polymers has been an area of great discussion, however, it still remains a controversial topic.\textsuperscript{47,48} The difficulty when trying to quantitatively measure energy migration is that the dynamics of conjugated polymers change drastically over time, whether it is within a polymer backbone or between neighboring chains. While it can be confidently said that energy transfer is occurring by both through-space (Förster) and through-bond (Dexter) mechanisms, it still remains debatable as to what mechanism is more dominant and therefore what would lead to a greater contribution. An understanding of energy migration is of importance when designing materials for chemo- and/or biosensing devices, excitonic photovoltaic cells or light-emitting devices. For example, due to the large exciton delocalization and rapid energy transfer observed in conjugated polymers, this makes them excellent candidates for sensing systems, which have been demonstrated by Swager utilizing the concept he termed as “signal amplification” that will be discussed in a future section. This section will discuss both through-space (Förster) and through-bond (Dexter) modes of energy transfer as they are applicable to conjugated polymers.

Conjugated polymers are inherently disordered materials, making it difficult to study their photoexcitation properties. As described previously, an ideal isolated conjugated polymer chain structure would exist as a planar molecule with complete delocalization along the backbone. Unfortunately, this is not a realistic picture of conformation in conjugated polymers, as they tend to contain macromolecular defects such as kinking, coiling, twisting, etc. While it has been widely accepted that upon excitation, an isolated conjugated polymer chromophore produces an intrachain exciton relying on orbital overlap,\textsuperscript{49} the idea becomes a lot less transparent when adjacent chromophores are in close proximity to each other, whether that be from segments of the same chain or other chains. This close proximity enables the interchain aggregate formation
that allows for delocalization of $\pi$-electrons between polymer segments through electrostatic coupling between transition dipoles.\textsuperscript{47} However, due to the short intermolecular separations (especially in thin-films) of chromophores, traditional approximations of electronic couplings are rendered insufficient in conjugated polymers.\textsuperscript{50} One major challenge is to account for the coupling between numerous $\pi$-orbitals that remain closely spaced in energy.

Previously, electronic energy transfer in conjugated polymers was primarily attributed to Förster energy transfer by dipole-dipole interactions of chromophores.\textsuperscript{51-53} Schwartz \textit{et al.} proved this through isolation of PPV chains into pores of an extended silica matrix.\textsuperscript{51} By isolating the chains, they could measure the exciton diffusion by polarized luminescence spectroscopy along the chain while inhibiting interchain interaction. They discovered that exciton diffusion was a slow process in intrachain energy migration due to weak dipole coupling along the backbone, ranging from tens of picoseconds to hundreds of picoseconds. Additionally, interchain energy transfer was discovered to be much faster from a picosecond to tens of picoseconds. Their studies into interchain interactions could also be explained through fluorescence spectroscopy experimentation.\textsuperscript{54} A primary signature of the spectrum in excited interchain chromophores in conjugated polymers is the bathochromic, or red-shifted emission as a result of delocalization between segments, lowering the energy relative to the isolated chain exciton. While this provides some insight into the contribution of through-space energy transfer qualitatively, this trademark provides an unclear distinction of interchain and intrachain species; especially since excitons in conjugated polymers have the ability to migrate towards low-energy interchain states from higher-energy intrachain states. This presents additional issues for energy transfer in conjugated polymers because interchain emission would also be quite difficult to detect as the lifetimes are shown to be long-lived resulting in low quantum yields.\textsuperscript{55}
Contrary as to what was believed to be a dominance of interchain energy transfer in conjugated polymers, Swager et al. demonstrated that the intramolecular energy transfer was indeed a major contributor during excitation of conjugated polymers in anisotropic Langmuir–Blodgett films of monolayered PPE. The insight into the contribution of the two mechanisms of intramolecular energy transfer was further explored in chain-extended conformations in nematic liquid crystals.

Figure 1.15. Simplified representation of conjugated polymer in isotropic and LC solutions. In isotropic solution, the conformational disorder in the polymer backbone prevents efficient intrachain exciton migration, thus resulting in predominant emission from the PPE backbone. In nematic LC solution, the electronic conjugation on the straightened and planarized polymer chains is higher, which leads to the enhanced intrachain exciton migration toward the terminal groups with a concomitant increase in the termini's emission. Reproduced with permission from Ref. 58. Copyright © 1998 American Chemical Society.

While intramolecular energy transfer by orbital overlap (Dexter mechanism) must overcome molecular defects such as twisting and coiling (and therefore was considered a non-essential contributor relative the through-space exciton hopping by Förster mechanism), nematic liquid crystals allowed for the enhancement of conjugation length while additionally limiting the amount of intermolecular interactions. Furthermore, by functionalizing terminal ends of the polymer chain with a low-energy unit, energy migration can be monitored intramolecularly by site-selective emission of the fluorescent capping agent when dissolved in a liquid crystal
solution. The fluorescence quantum yield observed demonstrated the efficiency and importance of the Dexter mechanism of the intramolecular energy transfer as fluorescence emission could also be diminished when temperature was raised above the nematic–isotropic transition therefore disrupting conjugation length.\textsuperscript{58}

Recently Lupton \textit{et al.} have elegantly described a method for quantitatively measuring the contribution of intramolecular energy migration in conjugated polymers through the use of cryogenic single chain spectroscopy.\textsuperscript{59-66} This allows observation of individual chromophores within a single polymer chain yielding narrow single-phonon transition lines at low temperatures. The analytical technique can differentiate between intermolecular, intramolecular and dynamic modes of disorder – in an attempt to conclusively tackle contributions of energy transfer in isolated chains upon excitation. What they found in P3HTs is that a single chromophore in the conjugated chain can adopt multiple conformations that affect the adjacent chromophore on a single chain through coherent oscillation, which also has a significant impact on intermolecular energy transfer.\textsuperscript{66} This is in good agreement with idea that conjugation length and orbital overlap of subsequent chromophores will dictate the degree of energy migration.

Upon comparison of these two mechanisms of energy transfer, it is evident that the Förster and Dexter mechanisms both contribute significantly to energy transfer in conjugated polymers. In the case of conjugated polymers, delocalization of \(\pi\)-electrons increases the range of Dexter energy transfer as the electronic coupling is preserved throughout the conjugated segments. However, Förster energy transfers controlling exciton migration both in solutions and solid-state is a strong possibility that can occur within the individual chains especially since there are defects of conjugation (kinks, chemical defects, coiling, etc.). It also remains a main mechanism of intermolecular energy migration at higher polymer concentration in solution, and partially in
aggregated and condensed systems (e.g. thin films). We will explore and discuss modes of energy transfer in conjugated polymers throughout this dissertation.

1.6. Practical Significance of Polythiophenes and Other Conjugated Polymers

Since conjugated polymers contain various length chromophores, this makes them useful materials in a myriad of optoelectronic devices. This section will attempt to discuss the importance and utility that these interesting materials offer to scientists and general population. In the previous section, energy transfer in conjugated polymers has been discussed, demonstrating the importance that molecular organization in solution has on excitonic applications. While traditionally silicon-based and other inorganic compounds have been used as semiconducting materials, in recent decades organic conjugated polymers have been slowly earning their way into the fabrication of next-generation devices.

1.6.1. Chemical and Biological Sensors.

One important application of conjugated polymers in chemical and biological sensing devices was first developed by Swager. These systems utilize the mechanism of fluorescence signal amplification where one binding event controls the fluorescence of the large fraction of the polymer chain due to the polymer acting as a “molecular wire” (Figure 1.16). One can see that the detection sensitivity would be increased due to the ability to amplify the change in electronic structure throughout the conjugated backbone. It is common to think of the conjugated backbone as a “molecular wire” transporting some carriers (in this case excitons). When an analyte binds to a receptor, this changes the energy levels of the polymer/analyte molecular orbitals, which ultimately elicits some amount of fluorescence quenching along the entire molecular wire. Therefore, the fluorescent signal amplification is due to the single binding event drastically altering the transport of the entire body of excitons.
Figure 1.16. Graphical representation of traditional vs. signal amplifying polymer chemical sensors upon binding of an analyte. Reproduced with permission from Ref. 67. Copyright © 1998 American Chemical Society.

One of the earliest examples of signal amplification in conjugated polymers was shown by Swager and Yang,\textsuperscript{68, 69} in which they explored the electronic perturbation of pentiptycene-derived phenyleneethynylene polymers by fluorescence quenching in thin-films.

Figure 1.17. TNT-detecting high free-volume conjugated polymers. Reproduced with permission from Ref. 68. Copyright © 1993 American Chemical Society.
In this case, the binding of the analyte 2,4,6-trinitrotoluene (TNT) vapor occurs by diffusion into the cavities of the polymer film as there is increased porosity through bulky pentiptycene moieties. Once the analyte is bound, fluorescence attenuation from the excited conjugated polymer to the electron acceptor TNT causes quenching of the fluorescent PPE polymer with increased sensitivity as compared to a small molecule sensor (Figure 1.17). There have been numerous other examples in recent literature where signal enhancement due to analyte binding sites that are lower in energy (“turn-on”) can be achieved as well as quenching enhancement where binding sites are higher in energy (“turn-off”). This would lead to advancement in optical detection of various analytes (usually present at very low concentrations) ranging from chemical warfare agents to biological markers.

1.6.2. Bulk-heterojunction Photovoltaic Cells.

One of the most important and sought after uses of conjugated polymers, and in particular poly(3-hexylthiophene), is their use in bulk-heterojunction (BHJ) photovoltaic cells. It has been shown that mixtures of an electron donating polymer (typically P3HT or PEDOT) and electron withdrawing compound (typically PCBM – a C_{60} derivative) create charge separation after exciting the donor molecule, leading to a conversion of light to electrical energy, which can be summed up in Figure 1.18.\textsuperscript{70} While we can see that this follows a similar mechanism of exciton generation and energy transfer discussed previously, when in a polymer blend of donor and acceptor compounds, the excitons generated after photoexcitation are split by the local electric field in to an electron-hole pair (typically referred to as a geminate pair) after exciton diffusion to the donor-acceptor interface.
This electron-hole pair at the interface needs an energetic driving force to overcome the Coulombic force and consequently split into separate charge carriers leading to charge transport and current generation.

1.6.3. Fluorescent Polymer Dots as Biological Imaging Agents.

Recently, conjugated polymer nanoparticles (colloquially known as polymer dots or Pdots), have been gaining interest in the fields of biology and medicine due to their highly fluorescent and tunable optical properties typically found in toxic and heavy metal-containing quantum dots (Qdots). While biological imaging agents must be chemically stable and highly fluorescent,
they would benefit from fluorescence in the near-IR (NIR) region as high-energy light has negative side-effects to cellular systems.

Pdots are traditionally produced by taking pre-synthesized polymers and dispersing them as colloids by either reprecipitation (McNeill et al.)\textsuperscript{72} or miniemulsification (Landfester et al.)\textsuperscript{73} processes, usually in the presence of surfactants. Recently, Mecking has developed charge-transfer Pdots via a Suzuki-Miyaura polymerization followed by reprecipitation, however they still require pre-synthesized polymers with aliphatic solubilizing side chains.\textsuperscript{74, 75} Although solubilizing conjugated polymers with side chains would lead to an increase in utility by increasing processability, for their use in Pdots it suffers from twisting of the planar backbone effectually decreasing the extent of delocalization as well as increasing the polymers propensity for oxidative degradation.

1.7. Research Focus

The main focus of this dissertation is the design of well-defined conjugated polymer architectures via transition metal-catalyzed controlled chain-growth polymerizations. A comprehensive review of controlled chain-growth catalyst transfer polymerizations discussed in this chapter exemplifies the importance and utility of these methods for the synthesis of complex macromolecular architectures important for next generation electronic and optoelectronic devices.

In Chapter 2, simple preparation of a novel Ni(II) external initiator for Kumada catalyst-transfer chain-growth polymerization used for the synthesis of conjugated polymers is described. The external initiator can be easily prepared by a direct oxidative addition of Ni(dppp)\textsubscript{2} to an aryl halide to afford a highly reactive catalytic initiator. The newly formed catalytic initiator bearing an aryl group can initiate controlled chain-growth polymerization of thienylmagnesium
monomers demonstrating the ability to control molecular weight while maintaining narrow molecular weight distribution. The aryl group associated with the catalyst can be incorporated on to the end-group of the growing polymer chain while, interestingly, we observe a halogen at the terminal end after quenching. Investigation into the mechanism of chain-growth polymerization and synthesis of well-defined block copolymers is described in this chapter as well.

Chapter 3 describes preparation of near-IR fluorescent conjugated nanoparticles synthesized directly from Grignard monomers in homogenous KCTP conditions. Unsubstituted monomers can be used to achieve higher stability and act as a means for the growing chain to precipitate as the polymer collapses onto itself when reaching a solubility threshold. Incorporation of a Ni(II) external catalytic initiator bearing a low-energy perylenedicarboximide (PDCI) unit results in the central low-energy fluorescent “core” in which the higher energy fluorescent “arms” can funnel energy towards. Details of energy transfer were studied by optical spectroscopy as well as transient absorption spectroscopy exhibiting a long lifetime typical of exciton migration.

In Chapter 4, a similar Ni(II) catalytic initiator with a low-energy PDCI unit has been used to prepare complex amphiphilic block copolymers with a PDCI core where energy transfer in isolated polythiophene chains can be investigated. The copolymers consisting of a central PDCI unit, hydrophobic poly(3-hexylthiophene) chains, and hydrophilic temperature-responsive poly(N-isopropylacrylamide) (PNIPAm) grafted polythiophene chains demonstrated supramolecular re-organization upon changing external stimulus such as solvent polarity or temperature. The change in optical properties and structural reorganization was explored by optical spectroscopy, electron microscopy, as well as small-angle neutron scattering (SANS) experiments.
In the concluding Chapter 5, novel class of cis- and trans-poly(phenylene ethynylene vinylene)s (PPEVs) conjugated polymers has been prepared using phosphine ligated Ru-complexes and NHC-ligated Pd-complex, respectively. While there have been practically no studies or preparation and properties of PPEVs, we filled this gap by carrying out preparation, structural characterization, and photophysical studies of these novel polymer materials.

1.8. References


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CHAPTER 2. ONE-STEP SIMPLE PREPARATION OF CATALYTIC INITIATORS FOR CATALYST-TRANSFER KUMADA POLYMERIZATION: SYNTHESIS OF DEFECT-FREE POLYTHIOPHENES

2.1. Introduction

Organic semiconducting polymers have emerged as materials of choice for electronic and optoelectronic applications (such as thin-film transistors, photovoltaic cells and polymer light-emitting diodes)\(^1\)-\(^3\) and chemo- and biosensing devices.\(^4\),\(^5\) Among semiconducting polymers, polythiophenes (PTs) hold a special place due to their excellent thermal and environmental stability, high conductivity in doped form, and possibility to adjust their optical and electronic characteristics by structural modifications.\(^6\),\(^7\) The pressing need to fine-tune the polymers’ properties to meet the requirements of particular applications necessitates searching for simple and efficient synthetic methods to prepare PTs and their copolymers, as well as other classes of semiconducting polymers, in a controlled manner and with precisely defined molecular composition. Living catalyst-transfer polymerization based on Ni-catalyzed Kumada coupling of 5-bromo-2-thienylmagnesium monomers became a well-established method for preparing PTs and their block copolymers\(^8\)-\(^11\) following the milestone discovery by McCullough\(^12\),\(^13\) and Yokozawa\(^14\),\(^15\) that this process occurs in a living chain-growth fashion. Over the recent years it has been a subject of detailed mechanistic studies, which revealed that the polymerization proceeds through a catalytic cycle mechanism involving a series of consecutive transmetalation – oxidative addition – reductive elimination steps in a manner similar to elementary steps in a typical transition metal catalyzed reaction, with strong dependence of the mechanism on the structure of catalyst.\(^16\)-\(^19\) Participation of an associative Ni(0)-arene \(\pi\)-complex as a key intermediate was proposed to explain the “living” character of the polymerization, however this

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intermediate has not been experimentally observed in the polymerization (although recent results by McNeil showed strong, albeit indirect, evidence in favor of participation of a Ni(0)-arene intermediate in the polymerization process\textsuperscript{20}). Typically, in order to stay within the “living” regime, the polymerization has to be carried out at ambient temperature, and, due to lower reactivity of the conventionally used Ni(II) catalysts (e.g. Ni(dppp)Cl\textsubscript{2}, where dppp is 1,3-bis(diphenylphosphino)propane), this generally yields polymers with low to moderate molecular weights and insufficient regioregularity.\textsuperscript{21-23} Furthermore, there is a prominent possibility of the occurrence of transfer of the propagating Ni(II) reactive center to another chain during polymerization,\textsuperscript{18} or chain termination by disproportionation,\textsuperscript{24} therefore the polymerization sometimes is described as quasi-“living”.\textsuperscript{13} Achieving truly “living” polymerization thus depends upon the availability of highly reactive universal catalytic systems. An important milestone was introduction, by Kiriy\textsuperscript{25, 26} and Luscombe,\textsuperscript{27} of externally initiated catalyst-transfer polymerization where stable aryl-Ni(II) initiating complexes, e.g. square-planar complex 2-1, could be used to carry out Kumada polymerization of Grignard monomer 2-3 to form PT polymers and block-copolymers with well-defined molecular composition (Scheme 2.1). Since initial reports, new more efficient catalysts for externally-initiated polymerization have been developed, as well as this approach has been extended toward other classes of important semiconducting polymers such as poly(\textit{p}-phenylene)s,\textsuperscript{28} polyfluorenes,\textsuperscript{29, 30} poly(\textit{p}-phenylene ethynylene)s,\textsuperscript{31} alternating copolymers\textsuperscript{32-34} and block copolymers,\textsuperscript{35-37} as well as some complex polymer architectures.\textsuperscript{38} In another important development, externally-initiated catalyst-transfer polymerization was used with surface-immobilized external initiators to prepare surface-attached brushes and thin films of semiconducting polymers.\textsuperscript{39-43} Thus, it looks obvious that externally initiated catalyst-transfer polymerization is superior in preparation of highly regioregular PTs, as
well as other classes of semiconducting polymers in a controlled manner. In all known cases, the best external catalytic initiators were square-planar Ni(II) complexes stabilized by bidentate phosphine ligands (such as complex 2-1), whereas using monodentate ligands (such as PPh₃) proved to yield catalytic initiators with poor performance.²⁵,⁴⁴

Scheme 2.1. Various routes to prepare external catalytic initiator in catalyst-transfer polymerization (X = Cl, Br) and its use to prepare PT by Kumada polymerization of Grignard monomer 2-3.

In conventional methods, preparation of the external catalytic initiators with bidentate ligands requires a relatively complicated synthetic procedure. In an earlier procedure developed by Luscombe,²⁷ oxidative addition of an aryl halide to a commercially available Ni(0) complex Ni(PPh₃)₄ resulted in a square-planar intermediate 2-2 (Scheme 2.1, route A). This was followed by ligand exchange between the intermediate 2-2 and dppp to form catalyst 2-1. This indirect method is relatively complex, low yielding, and results in contamination of the target polymerization catalytic initiator 2-1 with an undesired monodentate ligand PPh₃. Because external catalytic initiators containing monodentate ligands are inferior catalysts in the chain-growth Kumada polymerization, contamination with such ligands leads to less efficient
polymerization, with the resulting PT polymers having relatively low molecular weight. Furthermore, monodentate ligands may facilitate disproportionation and subsequent aryl-aryl homocoupling of the catalytic initiator. Senkovskyy et al. recently developed an alternative procedure which includes reaction of Ni(dppp)Cl₂ with sterically crowded Grignard reagents (Scheme 2.1, route B). This method is convenient in producing external catalytic initiator 1 but also suffers from the possibility of aryl-aryl homocoupling, and therefore is limited to sterically crowded aryl moieties (and also requires relatively complex work-up and purification procedure). So far the best approach available for the preparation of catalytic initiator 1 was developed by Kiriy. It starts with the reaction between an aryl halide and Et₂Ni(bipy) (where bipy is 2,2'-bipyridyl), and the intermediate complex is further converted to 2-1 via ligand exchange (Scheme 2.1, route C). This method enabled preparation of an uncontaminated and reactive external catalytic initiator, which was used to prepare highly regioregular defect-free poly(3-hexylthiophene), P3HT, via controlled chain-growth polymerization. However, Et₂Ni(bipy) is not easily available, unstable, and hard to handle (due to its high reactivity with moisture and oxygen), and the overall preparation still requires a more complex two-step procedure.

Obviously, the simplest direct approach to prepare uncontaminated catalytic initiators like complex 2-1 would be to employ oxidative addition of Ni(0) complexes with bidentate ligands (e.g. Ni(dppp)₂) to aryl halides (Scheme 2.1, route D). This, however, has never been accomplished because Ni(0) complexes with bidentate phosphine ligands were considered either unreactive toward aryl halides, or yielding complex mixtures of various by-products. In our search for a simpler method enabling preparation of pure and efficient external catalytic initiator like 2-1, we decided to investigate more closely direct oxidative addition of an easily
available\textsuperscript{49} and stable Ni(dppp)$_2$ to aryl halides as, if successful, this would produce external catalytic initiators in a highly-yielding simple route and uncontaminated with monodentate ligand or any other undesirable by-products. Indeed, generating Ni(II) external initiators by this direct method resulted in a highly efficient catalytic system for Kumada “living” polymerization, allowing simple preparation of defect-free PT polymers and block copolymers with high molecular weight in short reaction times. In this manuscript, we describe preparation by this novel method and properties of the resulting external catalytic initiators, and their application in chain-growth living polymerization, as well as some unexpected mechanistic consequences of using these catalytic initiators.

\section*{2.2. Results and Discussion}

2.2.1. Investigation of Oxidative Addition Reaction between Aryl-bromide and Ni(0).

Reaction of aryl halides with Ni(dppp)$_2$. In spite of the earlier reports and established consensus that Ni(0) complexes containing bidentate phosphine ligands do not react with aryl halides,\textsuperscript{47, 48} we decided to investigate the reaction between 5-bromo-2,2’-bithiophene 2-4 and Ni(dppp)$_2$ (Scheme 2.2A). Although not commercially available, Ni(dppp)$_2$ can be easily prepared in large scale using a simple literature procedure,\textsuperscript{49} and can be stored for a long time. The choice of bithienyl (rather than more typical phenyl or substituted phenyl) as an aryl species was prompted by the anticipated higher reactivity of the bithiophene-based catalytic initiator in chain-growth Kumada polymerization. For the reaction, an equimolar mixture of 2-4 and Ni(dppp)$_2$ was stirred in THF or toluene at 50 °C. The reaction was monitored by $^{31}$P NMR where Ni(dppp)$_2$ could be easily identified by a characteristic singlet at 12.8 ppm. In THF solvent, over a short period of time the formation of two doublets at approximately 19 and –3 ppm ($J_{P-P} = 66$ Hz) typical of the square-planar Ni(II) complex 2-5 was observed, and after 24 to
48 h reaction time the transformation was approximately 80% complete (Figure 2.1A). The transformation of bromide 2-4 to complex 2-5 was very clean, with essentially no by-products present in the reaction mixture (as was judged by $^1$H and $^{31}$P NMR spectroscopy).

![Diagram](image)

Scheme 2.2. Preparation of external catalytic initiators 2-5 and 2-7 by direct oxidative addition of Ni(dppp)$_2$ to aryl bromides, as well as by the ligand-exchange route.

In the case of toluene solvent, stirring the reaction mixture for 48 h at 50 °C resulted in substantial decrease of the initial $^{31}$P NMR singlet of Ni(dppp)$_2$ (when compared to the signal intensity of an external reference 80% H$_3$PO$_4$), but no new signals were observed (Figure 1B). When, however, the reaction mixture was concentrated in vacuo and the residual product redissolved in THF, in the $^{31}$P NMR spectrum we observed the same pair of doublets characteristic of the square-planar complex 2-5. Based on the intensity decrease of the signal of Ni(dppp)$_2$, we could estimate similar conversion to the complex 2-5 as in the case of using THF solvent.
Figure 2.1. (A) $^{31}$P NMR spectrum of the reaction between bithienyl bromide 2-4 and Ni(dppp)$_2$ in THF at 50 °C after 24 h. (B) $^{31}$P NMR spectrum of the same reaction at 50 °C in toluene (the NMR trace of the reaction mixture after 48 h reaction time was shifted for better clarity and does not correspond to the chemical shift scale at the bottom of the figure). For the reaction in toluene the spectra were acquired with 80% H$_3$PO$_4$ external reference for signal intensity calibration.

Thus, independent of the solvent, the reaction between 5-bromo-2,2'-bithiophene 2-4 and Ni(dppp)$_2$ cleanly produced Ni(II) catalytic initiator 2-5. Probably, the absence of NMR signals from 2-5 in toluene could be explained by deviation from the square-planar coordination of Ni(II) in the diamagnetic complex 2-5 due to steric repulsion between bithienyl and Br substituents resulting in the formation of a less planar structure with increased paramagnetic character (indeed, the extreme case of such deviation would be formation of a paramagnetic...
tetrahedral Ni(II) complex). We found similar distortion of the square-planar geometry in a single-crystal X-ray structure of a related compound Ni(dppp)Br$_2$ (Figure 2.2) which was obtained as a product of Ni(dppp)$_2$-promoted homocoupling of two molecules of 2-4 (vide infra).

![ORTEP image representing crystal structure of Ni(dppp)Br$_2$ showing distortion from square-planar configuration of Ni(II) center. The distortion of atom Br2 (and, to the lesser extent, of atom Br1) away from the plane derived by atoms Ni1, P1, and P2 is visible in the image.](image)

In good agreement with its somewhat paramagnetic character, Ni(dppp)Br$_2$ did not show any signals in its $^{31}$P NMR spectrum. In contrast to toluene solvent, the square-planar geometry of Ni(II) center can be better stabilized in THF due to strong ability of THF molecules to coordinate at the outer-sphere axial positions of the Ni(II) complex.

One remarkable feature of the reaction between bromide 2-4 and Ni(dppp)$_2$ was the absence of quaterthiophene 2-6 which would be a product of aryl-aryl homocoupling between two molecules of 2-4. Indeed, aryl-aryl homocoupling is a very common reaction of aryl halides occurring in the presence of equimolar amount of a Ni(0) complex.$^{50, 51}$
Scheme 2.3. Suggested mechanism of aryl-aryl homocoupling through disproportionation between two molecules of catalytic initiator 2-5.

Figure 2.3. UV-vis absorption spectra of the reaction mixture between bromobithiophene 2-4 and Ni(dppp)₂ in THF for 48 h at 50 °C corresponding to the 2.5 mM total concentration of catalytic initiator 2-5 (black trace). An arrow indicates a band corresponding to absorption of quaterthiophene (estimated concentration based on extinction coefficient e 36,000 M⁻¹ cm⁻¹ was 8.0 µM). The green trace shows a spectrum of 20 µM solution of quaterthiophene 2-6 in THF. Left and right y-axes correspond to initiator 2-5 and quaterthiophene 2-6, respectively.
Independent of whether the reaction between 2-4 and Ni(dppp)$_2$ was carried out in THF or toluene, analysis of the final reaction mixture by UV-vis spectroscopy (since quaterthiophene shows a distinct absorption band at 386 nm$^{52}$) revealed formation of less than 1% of 2-6 (Figure 2.3). Although no quaterthiophene was found when the reaction was carried out at 50 °C for 48 h, substantial amount of quaterthiophene 2-6 was formed when the reaction in toluene was carried out at 70 °C for 7 days. In addition to quaterthiophene, in such conditions we observed formation of a significant amount of dark-red crystalline precipitate of Ni(dppp)Br$_2$ (which was identified by single-crystal X-ray analysis). Formation of both quaterthiophene and Ni(dppp)Br$_2$ was consistent with disproportionation between two molecules of 2-5 followed by aryl-aryl homocoupling (Scheme 2.3).$^{24}$ Thus, it appears that aryl-aryl homocoupling was negligible at 50 °C but became a substantial reaction pathway at 70 °C – an interesting example of temperature control of the reaction course.

For comparison purposes, we also attempted to prepare the Ni(II) complex 2-5 following the ligand exchange route developed by Luscombe (Scheme 2.2A).$^{27}$ The product mixture was characterized by $^1$H and $^{31}$P NMR. Although the ligand-exchange route did result in the formation of 2-5, we also observed a significant amount of quaterthiophene 2-6 indicating the readily occurring homocoupling between two sterically unhindered bithienyl moieties. The abundance of the homocoupling product (standing in contrast with the absence of such a product in the case of direct reaction between 2-4 and Ni(dppp)$_2$) can probably be explained by facilitation of the coupling by Ni(PPh$_3$)$_4$ – a Ni(0) complex with a monodentate spectator ligand. Another typically related product – Ni(dppp)X$_2$ (where X is halogen from the initial aryl halide) – was also observed, thus pointing on disproportionation as the main homocoupling route. Since Ni(dppp)X$_2$ can catalyze non-externally initiated Kumada polymerization, some loss of the
“living” character (and lower molecular weight and worse regioregularity) would be a likely consequence of using the catalytic initiator prepared by this ligand-exchange procedure. In addition, the ligand exchange procedure resulted in significant presence of monodentate ligand PPh$_3$ in the final product (up to 50 % even after multiple reprecipitation attempts) which could have detrimental effect on the chain-growth polymerization. Therefore, preparation of 2-5 by direct reaction between aryl halide 2-4 and Ni(dppp)$_2$ has a clear advantage over the traditional schemes based on ligand exchange, and this advantage was critical in its performance in Kumada polymerization discussed below.

To better understand electronic nature of the catalytic initiator 2-5, we carried out electrochemical studies. Cyclic voltammograms (CVs) in THF solutions of complex 2-5 (prepared by direct reaction between bromide 2-4 and Ni(dppp)$_2$ as well as by the ligand exchange procedure as outlined in Scheme 2.2A), Ni(dppp)$_2$, and Ni(dppp)Br$_2$ are shown in Figure 2.4. The Ni(0) complex exhibited two reversible one-electron waves at $E_{1/2}$ 0.08 V and –0.66 V vs. Ag/Ag$^+$ electrode. These waves could be assigned to Ni(I/0) and Ni(II/I) couples, respectively. Both samples of complex 2-5 exhibited almost superimposable CV traces, with reversible waves at $E_{1/2}$ –0.71 V (directly prepared) or $E_{1/2}$ –0.76 V (prepared by ligand exchange) corresponding to Ni(II/I) couple, but practically no Ni(I/0) wave. Indeed, the position of the Ni(II/I) redox wave was similar to a redox peak of the reference complex Ni(dppp)Br$_2$ ($E_{1/2}$ –0.71 V). This result indicated that, independent of the preparation procedure, complex 2-5 was a Ni(II) species with a square-planar metal configuration.

Although a solution of 2-5 prepared by the reaction between 2-4 and Ni(dppp)$_2$ at 50 °C could be immediately used for initiation of Kumada polymerization (as it contained ~80% of 2-5, along with 1 eq. of released dppp ligand, small amounts of unreacted 2-4 and Ni(dppp)$_2$, and
trace dppp oxide), we also found useful to purify the catalyst by precipitation into hexanes. The precipitation could help to remove unreacted 5-bromo-2,2’-bithiophene 2-4, and only partially help in removing free dppp ligand and unreacted Ni(dppp)$_2$, however the latter two impurities could not interfere with subsequent Kumada polymerization (as Ni(dppp)$_2$ does not catalyze such a polymerization, vide infra). After precipitation, the collected solid could be dried in vacuo, and stored in a refrigerator at −30 °C for a few months with no detectable decrease in catalytic activity.

![Cyclic voltammograms of catalytic initiator 2-5 and related reference compounds. Data were acquired in THF solutions at 0.1 V s$^{-1}$ scan rate with a Pt button working electrode (diameter 2 mm).](image)

Figure 2.4. Cyclic voltammograms of catalytic initiator 2-5 and related reference compounds. Data were acquired in THF solutions at 0.1 V s$^{-1}$ scan rate with a Pt button working electrode (diameter 2 mm).

When needed, the solid could be redissolved in THF to yield a solution of the catalyst 2-5. We found that both solid and solutions of 2-5 were not particularly air-sensitive, and could be handled with reasonable precaution normally used with transition metal catalyzed reactions.

To check for the generality of the direct oxidative addition of Ni(dppp)$_2$ to aryl halides, we investigated reaction between chloro- and bromobenzene and Ni(dppp)$_2$ in THF (Scheme 2.2B).
In the case of bromobenzene, after 48 h of stirring the reaction mixture at 40 °C, we found the characteristic pair of doublets in $^{31}$P NMR spectrum at 22 and −3 ppm ($J_{P-P} = 46$ Hz) which could be attributed to the complex 2-7 with square-planar configuration of the Ni(II) center. The reaction was a little slower as compared to the case of 5-bromo-2,2′-bithiophene 2-4, as only approximately 40% conversion to 2-7 was observed. Nevertheless, the reaction was clean and resulted in no aryl-aryl homocoupling despite the lack of steric hindrance of the unsubstituted phenyl (quenching the reaction mixture with aqueous HCl and subsequent chromatography analysis revealed less than 1% of the homocoupling product biphenyl). Upon precipitation of the reaction mixture in hexanes the isolated solid product showed approximately 75% of the catalyst 2-7 by $^{31}$P NMR (with the rest mainly being unreacted Ni(dppp)$_2$ and free dppp ligand). In contrast, chlorobenzene produced no detectable product 2-7, and only starting materials were detected in the reaction mixture. Thus, we concluded that in contrast to previous literature reports, oxidative addition between Ni(0) complex Ni(dppp)$_2$ and aryl bromides (as well as iodides but not chlorides) is a general reaction. Unlike previous approaches to catalytic initiators for catalyst-transfer Kumada polymerization, this method does not produce aryl-aryl homocoupling products even with sterically unhindered aryl groups, nor it results in contamination with any other undesired by-products. Since formation of bithiophene-based catalyst 2-5 was a clean and high-yielding process, in addition to high reactivity of the catalyst 2-5 in Kumada polymerization, this made it a natural choice for further polymerization studies.

2.2.2. Kumada Catalyst-transfer Polymerization Catalyzed by Complexes 2-5 and 2-7.

The most important application of aryl-Ni(II) complexes like 2-5 is using them as external catalytic initiators in chain-growth catalyst-transfer Kumada polymerization of 5-bromo-2-thienylmagnesium monomers to prepare polythiophenes. Therefore, we studied 2-5 as a catalytic...
initiator for polymerization of 5-bromo-4-hexyl-2-thienylmagnesium chloride 2-3. Typically, the Grignard monomer 2-3 is prepared by reaction between 1 equivalent of a sterically hindered Grignard reagent (e.g. isopropylmagnesium chloride) and 1 equivalent of 2,5-dibromo-3-hexylthiophene. We found experimentally (and this finding was in agreement with previous literature data53) that using exactly 1:1 ratio of dibromothiophene to i-PrMgCl did not result in complete conversion to 2-3 even after prolonged reaction time.

Scheme 2.4. Preparation of various polythiophenes by externally initiated Kumada polymerization. The polymers chains were mainly Br-terminated, although fractions of H-terminated chains were also observed in some cases.
Thus, as a matter of practical convenience, we found that using i-PrMgCl in a slight excess (1.1 equivalent) enabled achieving complete conversion to 2-3 (actually ~75% of 2-3 and 25% of its polymerization-unreactive regioisomer, as was determined by $^1$H NMR analysis after quenching the reaction mixture with water) in 1 h reaction time at 0 °C. The small residual amount of unreacted i-PrMgCl did not affect the living polymerization (vide infra), and therefore this method can be recommended as a practically convenient way to prepare Grignard monomer 2-3 from an easily available dibromothiophene starting material.

Table 2.1. Characterization of polythiophenes prepared by externally initiated catalyst-transfer Kumada polymerization.$^{a,b}$

<table>
<thead>
<tr>
<th>Entry</th>
<th>Polymer</th>
<th>Catalyst (mol%)</th>
<th>Yield, %</th>
<th>$M_n$ kDa</th>
<th>$M_n$ (calc) kDa</th>
<th>$M_n$ (GPC) kDa</th>
<th>$M_w/M_n$</th>
<th>%HT $^{d}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2-9 (P3HT) $^e$</td>
<td>2-5 (0.3)</td>
<td>76</td>
<td>55.3</td>
<td>60.0</td>
<td>1.47</td>
<td>100</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>2-9 (P3HT) $^e$</td>
<td>2-5 (0.5)</td>
<td>71</td>
<td>33.2</td>
<td>45.3</td>
<td>1.43</td>
<td>100</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>2-9 (P3HT) $^e$</td>
<td>2-5 (1.0)</td>
<td>74</td>
<td>16.6</td>
<td>26.7</td>
<td>1.53</td>
<td>100</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>2-9 (P3HT) $^f$</td>
<td>2-5 (1.0)</td>
<td>75</td>
<td>16.6</td>
<td>24.0</td>
<td>1.54</td>
<td>100</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>2-9 (P3HT) $^e$</td>
<td>2-5 (3.0)</td>
<td>77</td>
<td>5.5</td>
<td>10.1</td>
<td>1.72</td>
<td>100</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>2-10 $^e$</td>
<td>2-5 (1.0)</td>
<td>69</td>
<td>40.8</td>
<td>41.0</td>
<td>1.41</td>
<td>100</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>2-11 $^e$</td>
<td>2-5 (1.0)</td>
<td>72</td>
<td>40.8</td>
<td>41.0</td>
<td>1.46</td>
<td>100</td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>2-12 (P3HT) $^e$</td>
<td>2-7 (1.0)</td>
<td>66</td>
<td>16.6</td>
<td>27.0</td>
<td>1.25</td>
<td>100</td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>2-12 (P3HT) $^f$</td>
<td>2-7 (1.0)</td>
<td>73</td>
<td>16.6</td>
<td>24.0</td>
<td>1.16</td>
<td>100</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>2-13 (P3HT) $^e$</td>
<td>2-5 (1.0)</td>
<td>55</td>
<td>16.6</td>
<td>16.9</td>
<td>2.00</td>
<td>100</td>
<td></td>
</tr>
<tr>
<td>11</td>
<td>2-14 (P3HT) $^e$</td>
<td>2-7 (1.0)</td>
<td>40</td>
<td>16.6</td>
<td>14.0</td>
<td>1.75</td>
<td>100</td>
<td></td>
</tr>
</tbody>
</table>

$^a$ Data were obtained for crude polymer samples, without additional purification; $^b$ The Grignard monomers used for polymerization were prepared by reacting 1.1 eq. of i-PrMgCl with 1 eq. of the corresponding dibromothiophene at 0 °C for 1 h, except entries 10 and 11, where 1 eq. of i-PrMgCl was used; $^c$ Relative to polystyrene standards; $^d$ Determined by $^1$H NMR; $^e$ Reaction was quenched with methanol; $^f$ Reaction was quenched with 5 M HCl.
Adding a catalytic amount of catalyst **2-5** (1 mol%) to a solution of **2-3** in THF and allowing them to react for 1 h at 35 °C, followed by precipitation of the reaction mixture into methanol, produced completely regioregular poly(3-hexylthiophene) (P3HT) **2-9** (Scheme 2.4). The percent regioregularity in poly(3-alkylthiophene)s refers to the fraction of head-to-tail (HT) coupled repeating units; thus a 100% regioregular PT has 100% of HT coupling, whereas a polymer with low percentage of HT coupling (50-80%) would be considered regiorandom.\textsuperscript{54,55}

![Figure 2.5](image)

Figure 2.5. (A) GPC elution traces for P3HT polymers **2-9** prepared by varying the amount of catalytic initiator **2-5** added to a solution of Grignard monomer **2-3**. Solid traces correspond to samples prepared by quenching the reaction mixture with methanol, dash trace – quenched with 5 M HCl. (B) Experimental and calculated dependence of number average molecular weight ($M_n$) of **2-9** from the reciprocal molar fraction of catalytic initiator **2-5** (solid line represents linear fit of experimental data, $R^2 = 0.954$; dash line – calculated dependence). $M_n$ was determined by GPC relative to polystyrene standards.

The percent regioregularity is normally determined by careful integration of the two signals between 2.4 and 3.0 ppm in $^1$H NMR spectra; these signals belong to α-CH$_2$ protons of the 3-alkyl chains and ratio of their integral intensities serves as a reliable measure of regioregularity of 3-alkyl substituted PTs.\textsuperscript{56,57} As can be seen from the $^1$H NMR spectrum of **2-9**, there was only one peak in this region (a triplet at 2.80 ppm) which corresponded to HT junction, and the
essential absence of other peaks reflected 100% regioregularity of 2-9. The 100% regioregularity of 2-9 was also confirmed by the single aromatic peak at 6.98 ppm corresponding to HT junction, and the absence of lower-field signals in the aromatic region corresponding to other junction types.\textsuperscript{46}

In multiple experiments, we consistently prepared P3HT 2-9 with number average molecular weight ($M_n$) ranging from 10 kDa to 80 kDa, depending on the molar fraction of catalyst 2-5. In all the cases, obtained P3HT polymers were essentially defect-free (100% regioregularity) and were characterized by narrow polydispersity index, PDI ($M_w/M_n < 2$) even in crude samples, without any additional purification steps. The strongest evidence in favor of living chain-growth polymerization catalyzed by 2-5 was the fact that the molecular weight of P3HT 2-9 was linearly dependent on the reciprocal molar fraction of 2-5 taken for polymerization (Figure 2.5 and Table 2.1, entries 1-5). Experimentally (GPC) obtained number average molecular weights ($M_n$) were somewhat higher than theoretically predicted $M_n$'s, yet experimentally obtained molecular weights fell on the straight line with the slope identical to the theoretical prediction (Figure 2.3B). The higher GPC molecular weights of the polymer 2-9 relative to the theoretically predicted weights were reproducibly obtained in all polymerization runs. In a not perfectly “living” Kumada catalyst-transfer polymerization, experimentally obtained molecular weights would be lower than the theoretically predicted ones. The lower molecular weights originate from occasional chain transfer occurring through catalytic metal center migration from a growing polymer chain to a monomer in solution, which initiates a new polymer chain. The increased molecular weight, in this sense, reflects an exceptionally “living” character of the polymerization catalyzed by 2-5. An apparent “increase” could be related to a known overestimation of the molecular weights by polystyrene-calibrated GPC which becomes particularly significant at
lower molecular weights (but turns into underestimation at particularly high molecular weights).\textsuperscript{30} This may introduce a systematic error which can explain why both experimentally found and theoretically calculated $M_n$ datasets fell on parallel straight lines in the $M_n$ vs. $1/[2-5]_0$ plot (Figure 2.5B).

![Figure 2.6](image)

Figure 2.6. (A) Number average molecular weight ($M_n$) and polydispersity index (PDI) of polymer 2-9 as function of the monomer 2-3 percent conversion (solid line – calculated data). (B) $M_n$ of 2-9 as function of polymerization time. Polymerization was carried out with 0.25 mol \% of 5; $M_n$ and PDI ($M_w/M_n$) were determined by GPC relative to polystyrene standards, and percent conversion was determined by $^1$H NMR.

Linear dependence of the 2-9’s number average molecular weight $M_n$ on Grignard monomer 2-3 conversion (Figure 2.6A) also reflected the living chain-growth mechanism of polymerization. Furthermore, the polymerization was indeed rapid and efficient; it was practically complete in 20 min after addition of 2-5 to the Grignard monomer (Figure 2.6B).

We found some tendency for the polymers to undergo disproportionation upon quenching of the polymerization reaction mixture with methanol, which resulted in pronounced higher molecular weight shoulders in GPC traces (Figure 2.5A). The intensity of these shoulders increased proportionally to the catalyst 2-5 loading, which was likely related to the larger number of initiating sites increasing the propensity for the disproportionation to occur. This
phenomenon has been observed previously\textsuperscript{53,59,60} and is seemingly facilitated by quenching the polymerization reaction mixture with methanol. Indeed, we found that quenching the polymerization mixture with 5 M HCl (instead of methanol) produced 2-9 with almost the same molecular weight and polydispersity but without the higher molecular weight shoulder (Figure 2.5A and Table 2.1, entries 3 and 4).

One of the essential characteristics of a truly living polymerization is the possibility to prepare block copolymers by sequential addition of different monomers to the reaction mixture and allowing them enough time to react completely. By adding Grignard monomers 2-3 and 2-8 to a solution of the external catalytic initiator 2-5 (1 mol\%) at 35 °C, we prepared two completely regioregular (~100\% HT coupling within each block) block copolymers 2-10 and 2-11 with high molecular weights and in short polymerization times (Scheme 2.4 and Table 2.1, entries 6 and 7). The GPC traces for both block copolymers showed essentially monomodal narrow distribution of molecular weights, which was consistent with living character of the polymerization where all the initially formed reactive chains were active through the entire polymerization process. In preparation of block copolymers by chain-growth polymerization, it is critical to ensure complete consumption of the first monomer before addition of the second monomer (otherwise the second block would become a random copolymer of both monomers). The requirement of complete consumption of the first monomer (particularly at a high conversion when the reaction slows down) requires a polymerization reaction to be highly efficient. Catalytic initiator 2-5 prepared by direct reaction between 2-4 and Ni(dppp)\textsubscript{2} perfectly satisfies this requirement. Indeed, the homogeneous molecular composition of both blocks in 2-10 and 2-11 was unambiguously supported by clean and sharp \textsuperscript{1}H NMR peaks corresponding to aromatic hydrogens.\textsuperscript{61} Beyond serving as a demonstration of living character of this
polymerization and its synthetic versatility in controlled preparation of conjugated copolymers, the block copolymers 2-10 and 2-11 will be further converted into temperature-responsive poly(N-isopropylacrylamide)-grafted amphiphilic PTs for our ongoing studies of energy migration in conjugated polymers.  

We also tested phenyl-Ni(II) catalytic initiator 2-7 in polymerization of the Grignard monomer 2-3. As expected, this produced highly regioregular Ph-terminated P3HT 2-12 in a living chain-growth polymerization (Scheme 2.4 and Table 2.1, entries 8 and 9)). Therefore, the choice of an actual catalyst for polymerization (and aryl halide as a starting material for the catalyst) is mostly dictated by the terminal group which needs to be incorporated, whereas catalytic reactivity is not strongly dependent on the aryl halide choice.

To determine if the small excess of i-PrMgCl used in preparation of Grignard monomers 2-3 and 2-8 (Scheme 2.4) could affect the living polymerization, we also studied externally-initiated (with 1 mol% of catalytic initiators 2-5 or 2-7) polymerization of Grignard monomer 2-3 prepared using exactly 1 equivalent of i-PrMgCl. The total yield of the polymers obtained in this way (polymers 2-13 and 2-14 in Table 2.1) was lower, and they were characterized by somewhat smaller molecular weights and broader polydispersities (relative to the same polymers derived from Grignard monomer 2-3 prepared with 1.1 equivalent of i-PrMgCl), which was consistent with the presence of unreacted 2,5-dibromo-3-hexylthiophene which probably acted as a chain transfer reagent in the polymerization. Thus, using small excess of i-PrMgCl to prepare Grignard monomers for polymerization deems practically convenient, and results in robust living polymerization. On the other hand, using large excess of i-PrMgCl (e.g. 2 equivalents) to generate Grignard monomer 2-3 yielded P3HT polymers with low molecular weights (around 4
kDa when 1 mol% of 2-5 or 2-7 was used). Clearly, the large excess of unreacted \textit{i}-PrMgCl was detrimental for living polymerization.

To further evaluate the possible role of residual Ni(dppp)$_2$ present in the catalyst solution, we attempted to carry polymerization of 2-3 catalyzed by Ni(dppp)$_2$ in the conditions similar to those used in polymerization with catalysts 2-5 or 2-7. As expected, no polymerization occurred, and even after prolonged reaction time, only a low yield (less than 5%) of short oligomers was obtained. Thus, Ni(dppp)$_2$ (which was always present as a small impurity in the reaction mixture due to incomplete reaction of the formation of 2-5 or 2-7) was not capable itself of promoting polymerization.

2.2.3. Further Details on the Mechanism of Kumada Polymerization Catalyzed by Directly Prepared Complexes 2-5 and 2-7.

The mechanism of externally initiated catalyst-transfer chain-growth Kumada polymerization of Grignard monomer 2-3 is well established and includes a consecutive series of transmetalation, reductive elimination, and oxidative addition (Scheme 2.5). The Ni(0) intermediates II and IV$\pi$ formed in the reductive elimination steps remain bound to the PT chain through formation of a $\pi$-complex, and the Ni(0) center migrates intramolecularly to the terminus of the growing polymer chain, where it undergoes oxidative addition to the C–Br bond. Interestingly, as was convincingly demonstrated by Kiriy,$^{26}$ the Ni(0) migration is not exclusively unidirectional (toward the nearest C–Br polymer chain end), but the metal center can randomly walk in any direction, especially with higher molecular weight polymer chains. The mechanism of polymerization as well as structure of the intermediates should be reflected in the end group composition of the polymer chains which can be studied by mass spectrometry (MALDI-ToF) and $^1$H NMR end-group analysis.
Scheme 2.5. Mechanism of externally-initiated Kumada catalyst-transfer polymerization leading to regioregular poly(3-alkylthiophene)s with Ar/H and Ar/Br terminations.

We thoroughly studied the end group composition in the P3HT polymers obtained by polymerization of Grignard monomer 3 in the presence of 1 mol% of catalytic initiators 2-5 and 2-7. To account for possible variations of end-group composition due to quenching conditions, we prepared two polymer samples for each initiator by dividing the reaction mixture on two equal portions, and quenching each portion either with methanol or with 5 M HCl (which are shown as entries 4-5 and 8-9 in Table 2.1). For the end group analysis, all four polymer samples were thoroughly purified by extraction in a Soxhlet apparatus successively with methanol, hexanes, and chloroform, and chloroform fractions were used in the study. With both initiators,
incorporation of aryl terminal groups in all PT chains was evident from $^1$H NMR spectra of the purified polymers which displayed distinct signals from bithienyl or phenyl end groups. When the polymerization was initiated with bithiophene (biTh) catalyst 2-5, MALDI-ToF analysis showed predominant biTh/Br termination in the case of methanol quenching, and approximately equal distribution of biTh/Br and biTh/H terminated chains in the case of HCl-quenched polymer (Figure 2.7, A and B). Since MALDI-ToF data mainly reflect composition of lower molecular weight fractions, we also studied $^1$H NMR spectra which provide better overall representation of the high molecular weight polymer samples. Figures 2.8C and 2.8D show expanded fragments of $^1$H NMR spectra corresponding to the area of signals of $\alpha$-CH$_2$ protons. Two small triplets around 2.6 ppm are attributed to $\alpha$-CH$_2$ protons of the terminal 3-hexylthien-2,5-diyl unit in regioregular P3HT. Of these two triplets, a more downfield one corresponds to H-terminated chains whereas a more upfield signal originates from Br-terminated P3HT chains. The intensity ratio between these two signals was in a good agreement with the MALDI-ToF data thus indicating dominating Br termination of one chain end in both polymer samples independent of the polymerization quenching method. This finding was in clear contrast with previous data on chain-growth Kumada catalyst-transfer polymerization where almost exclusive Ar/H terminated PT chains had been observed.

The unexpected predominance of biTh/Br-terminated chains prompted us to look more closely at the reactive species existing during the polymerization. For this purpose, the polymerization of Grignard monomer 2-3 was carried out in an NMR tube with 18 mol% of 2-5 in order to obtain sufficient $^{31}$P NMR signal (Figure 2.8). Adding monomer 2-3 to the catalyst 2-5 caused no change in chemical shifts of the two doublets at 18 and –3 ppm characteristic of Ni(II) square-planar complex 2-5 but made them much sharper and better resolved.
Figure 2.7. Fragments of MALDI-ToF (A and B) and $^1$H NMR (C and D) spectra showing signal assignments for P3HT 2-9 prepared with 1 mol% of bithiophene initiator 2-5 upon quenching with methanol (A and C) and with 5 M HCl (B and D). Spectra A and C correspond to polymer in entry 3, and B and D – entry 4 in Table 2.1. $^1$H NMR spectra were acquired at 500 MHz in CDCl$_3$.

In addition, a clear signal appeared at –18 ppm characteristic of free dppp ligand, as well as a small broad signal near 17 ppm (Figure 2.8). This observation was in agreement with complex IV$\sigma$ being likely the dominating species during the polymerization (Scheme 2.5). The persistence of square-planar Ni(II) reactive complex IV$\sigma$ during polymerization was consistent with previous experimental studies by McNeil who observed similar Ni(II) square-planar complex as the resting state for Ni(dppp)Cl$_2$-catalyzed chain-growth polymerization of 2-3.$^{17}$ The $^{31}$P NMR spectrum did not change even after prolonged reaction time, but post-polymerization quenching the reaction mixture with methanol immediately resulted in disappearance of the signals.
Figure 2.8. $^{31}$P NMR monitoring of the polymerization reaction of Grignard monomer 2-3 catalyzed by the external catalytic initiator 2-5 (in THF). Black trace – catalytic initiator 2-5 before addition of monomer 2-3; blue trace – 5 min after adding monomer 2-3, and red trace – 1 h after adding monomer 2-3.

The persistence of the square-planar Ni(II) active species during the polymerization makes even more difficult to explain the predominant Br termination of the polymer chains. Indeed, protolysis of the Ni(II) reactive center in the intermediate IVσ upon treatment with a protic solvent or a strong acid was supposed to deliver H-terminated polymer chains, in agreement with numerous previous studies. Thus, a major fraction of the polymer chains prior to quenching likely did not have terminal Ni(II) species but was Br-terminated. If this were the result of an
active Ni center loss due to Ni(0) diffusion to another chain, this would reflect an essentially
non-“living” polymerization with all its consequences such as low molecular weight and broad
polydispersity of the product polymer.\textsuperscript{18} In contrast to this, in our case the polymerization was
undoubtedly “living” and thus chain transfer was a negligibly minor pathway. Locklin recently
suggested that disproportionation between two growing Ni(II)-terminated chains could be
responsible for increased molecular weight and end-group discrepancies.\textsuperscript{24} Disproportionation,
however, was unlikely to be involved in our case as this would result in biTh/biTh chain
termination which was not experimentally observed. A plausible explanation would be that the
square-planar Ni(II) intermediate $\text{IV} \sigma$ during polymerization remained in equilibrium with a
Ni(0) $\pi$-complex $\text{IV} \pi$ where Ni(0) center migrated into the PT $\pi$-electron conjugated chain. This
would be consistent with the idea of “random walk” of the Ni(0) associated $\pi$-complex as was
proposed by Kiriy.\textsuperscript{26} The residual Ni(0) complex Ni(dppp)$_2$ present in the catalyst solution could
possibly facilitate the process of forming a migrating Ni(0) $\pi$-complex at the PT backbone.
Indeed, experimentally observed presence of dppp signal in the $^{31}$P NMR spectrum of the
reaction mixture during polymerization could reflect dissociation of one dppp ligand from
Ni(dppp)$_2$ required for the formation of a PT-bound $\pi$-complex. Furthermore, the broad signal at
17 ppm observed in the $^{31}$P NMR spectrum in the course of polymerization could indeed be the
signal corresponding to the Ni(0) $\pi$-complex itself. The low intensity of this signal (and absence
of a strong evidence in favor of assignment of this signal as originating from the $\pi$-complex) may
make this explanation less credible; on the other hand, if the migration of Ni(0) center along the
PT backbone was fast in the NMR time scale, the $\pi$-complex’s NMR signal could become broad
or of low intensity, or even disappear. Indeed, despite being postulated as a key intermediate in
catalyst-transfer chain-growth polymerization, Ni(0) \( \pi \)-complex has never been directly observed and still remains an elusive species avoiding experimental detection.\(^6^3\)

Similar to polymerization initiated by the bithiophene catalyst 2-5, PTs prepared via initiation with phenyl catalyst 2-7 also showed predominantly Ph/Br termination both after methanol and 5 M HCl quenching. Thus, these results were consistent with potential intermediacy of Br-terminated \( \pi \)-complex IV\( \pi \) as a general reaction pathway. It is possible that unreacted excess of \( i \)-PrMgCl could eventually metalate the C–Br end of the complex IV\( \pi \) during the polymerization process, which upon quenching with a proton source would yield H-terminated chains.\(^5^3\) Indeed, polymers 2-13 and 2-14 prepared with no excess of \( i \)-PrMgCl showed almost exclusive Ar/Br termination both after methanol and 5 M HCl quenching. In contrast, polymerization using Grignard monomer 2-3 prepared with large (2 equivalents) excess of \( i \)-PrMgCl produced polymers with predominant Ph/H termination thus confirming possible metalation of the C–Br terminus in the intermediate complex IV\( \pi \). At this point, we cannot offer more details on the mechanism leading to the predominant Ar/Br terminated polymer chains. Nevertheless, the ability to obtain Br-terminated polymer chains in the course of a chain-growth catalyst-transfer polymerization (rather than typically observed H-termination) may have some practical significance as the Br site can be used for further functionalization of the polymer.

2.3. Conclusions

In contrast to the widely established opinion that Ni(0) complexes with bidentate phosphine ligands are inert toward aryl halides, we have developed a simple procedure for preparation of efficient catalytic initiators for catalyst-transfer Kumada polymerization by direct oxidative addition between easily available Ni(dppp)\(_2\) and aryl halides. In addition to experimental simplicity of this procedure, absence of monodentate ligands (required in conventional
preparation procedures based on ligand exchange) eliminated typical side reactions (such as aryl-aryl homocoupling), and was responsible for high yield and good stability of the catalytic initiators. High reactivity of these initiators enabled highly efficient and rapid preparation of thiophene polymers and block copolymers in living chain-growth Kumada polymerization of 5-bromo-2-thienylmagnesium monomers. An interesting feature of the polymerization catalyzed by these Ni(II) initiators was that it produced PT chains with predominant Ar/Br termination (Ar = biTh or Ph). While clear understanding of the fine mechanistic features leading to Br-termination requires further studies, it does indicate the uniqueness of the polymerization in this case, as well as reflects complexity of the chain-growth catalyst-transfer mechanism where many details still remain unexplored. From a practical standpoint, our approach offers the simplest and highly efficient way to control preparation of complex PTs as well as other conjugated polymers and copolymers (we have some initial evidence that it can be used in polymerization of various aromatic monomers). Furthermore, the efficient living polymerization can be used not only for the preparation of conjugated polymers in solution, but also in the preparation of surface-immobilized films of conjugated polymers by using surface-bound initiating species. This intriguing possibility is being currently investigated.

2.4. References


(60) Miyakoshi, R.; Yokoyama, A.; Yokozawa, T. Development of catalyst-transfer condensation polymerization. Synthesis of π-conjugated polymers with controlled


3.1. Introduction

Conjugated polymer nanoparticles (NPs) occupy an important niche in materials science due to their tunable optical properties well-suited for applications in biomedical imaging, sensing, light-emitting diodes, photovoltaics, etc.\textsuperscript{1,2} Bright fluorescent conjugated polymer dots (Pdots) show some advantages over more traditional inorganic nanoparticles (quantum dots), mainly due to the polymer particles’ low cost, tunability of spectroscopic properties by structural modifications of the polymer, availability in various sizes, as well as the low toxicity.\textsuperscript{2-5} Unlike the inorganic quantum dots which are most typically synthesized in solution starting from small-molecule reactants, the two most popular approaches to prepare Pdots require first synthesizing a soluble conjugated polymer (CP) to be subsequently used in nanoparticles preparation. In the dispersion (reprecipitation) technique, pioneered during the last decade by McNeill, the nanoparticles are prepared by injecting a dilute solution of a CP in a water-miscible organic solvent (e.g. THF) to water upon rapid mixing.\textsuperscript{6-8} In the miniemulsion method, nanoparticle preparation starts with making a surfactant-stabilized aqueous emulsion of a conjugated polymer solution in a water-immiscible organic solvent (e.g. chloroform) followed by evaporating the organic solvent.\textsuperscript{9-11} Less commonly, conjugated polymer nanoparticles can be prepared via step-growth polymerization of properly functionalized monomers in stabilized organic-aqueous miniemulsions, followed by post-polymerization evaporation of the organic solvent. For example, Mecking et al. described preparation of fluorescent CP nanoparticles via transition metal catalyzed polymerizations in miniemulsion.\textsuperscript{12-14} Although the latter process provides better control over composition and functionality of polymer nanoparticles, the requirement for
the polymerization to be carried out in aqueous emulsions puts substantial limitation on the scope of applicable chemical reactions which can tolerate such polymerization conditions. In addition, none of the previously developed approaches allow preparation of more complex nanostructures such as conjugated polymer “core-shell” nanoparticles.

![Diagram](image)

Figure 3.1. Preparation of single-molecule conjugated polymer nanoparticles via living chain-growth polymerization in solution. Blue circles represent active catalytic sites for polymerization.

Rather than relying on pre-synthesized soluble CPs or heterogeneous organic-aqueous emulsions for preparation of organic CP nanoparticles, we propose a different approach based on synthesizing conjugated polymer nanoparticles in homogeneous reaction conditions directly from small-molecule monomers via using externally initiated controlled living polymerization (Figure 3.1). In this method, a solution of a catalytic initiator functionalized with minimum two (or more) active catalytic sites is added to a solution of a properly functionalized monomer to initiate the polymerization. Due to living character of the polymerization, the polymer growth will be occurring uniformly from all the catalytic sites as long as the in situ formed macromolecular system remains soluble in the reaction conditions. It has been previously demonstrated that CPs such as regioregular poly(3-alkylthiophene)s in good solvents adopt a helical conformation with 12 thiophene units in each turn of the helix.\(^{15}\) Thus, the CP “arms” growing from the catalytic initiator would tend to helically coil around the initiator. After the macromolecule has grown beyond the solubility limit in the given conditions, it will collapse
from solution as a nanoparticle, which will be facilitated by the “arms” coiling, and the further growth in the now heterogeneous conditions will likely slow down (or completely stop). Once precipitated, these nanoparticles can be redispersed in either organic or aqueous medium forming a stable colloidal suspension for further applications. Ideally, since the particle size in such a scheme is predominantly controlled by solubility of the polymer system in a given solvent, one would expect uniform size of the nanoparticles independent of the reaction time, and the possibility to adjust the nanoparticle size by varying solubilizing groups on the monomer or changing the solvent to carry out polymerization. Preparation of nanoparticles by this approach would occur as a homogeneous solution reaction in a non-aqueous organic solvent (instead of organic-aqueous emulsions), and therefore would tolerate many different polymerization reactions which are incompatible with aqueous conditions (e.g. organometallic reagents). In addition to efficiency and practical simplicity, this approach would enable convenient tuning of the photophysical properties of the nanoparticles via preparation of “core-shell” structures if a proper chromophore “core” is chosen as a catalytic initiator. Also, the solution-grown organic nanoparticles would show high structural stability, including tolerance to organic solvents (which is not the case for CP Pdots made by conventional reprecipitation or miniemulsion methods), as well as increased photostability. This stability would be primarily related to the absence of solubilizing side groups on the CP chains, as alkyl side groups act as primary initiating sites for photo- and thermal degradation of CPs.\textsuperscript{16,17} The solvent tolerance of the nanoparticles would be particularly beneficial if further processing of the initially prepared nanoparticles is required (e.g. further functionalization, or using the NPs as part of more complex device architectures, etc.). Despite the potential advantages of the direct solution polymerization approach, to the best of our knowledge it has not been explored in the preparation of conjugated polymer nanoparticles.
In this paper, we demonstrate using the externally initiated living polymerization approach in a simple and efficient preparation of polythiophene (PT) and poly-\(p\)-phenylene (PPP) nanoparticles which incorporate a low energy gap perylenedicarboximide (PDCI) “core” and exhibit fluorescence both in the visible and near-infrared spectral regions.

3.2. Results and Discussion

Successful implementation of this new approach requires availability of a suitable living polymerization chemistry. Living catalyst-transfer polymerization based on Kumada coupling of halogen-substituted arylmagnesium monomers became an important tool for the controlled preparation of conjugated polymers,\(^{18-22}\) especially following recent development of its externally initiated version, most notably by Kiriy,\(^{23,24}\) Luscombe,\(^{25}\) and others.\(^{26-28}\) Recently, we described a simple preparation of efficient catalytic initiators for Kumada catalyst-transfer polymerization (KCTP) based on the reaction between aryl bromides and Ni(0) complex Ni(dppp)\(_2\) (where dppp is 1,3-bis(diphenylphosphino)propane).\(^{29}\)

![Scheme 3.1. Synthesis of PDCI-PT and PDCI-PPP nanoparticles via solution Kumada catalyst-transfer polymerization, as well as preparation of control compounds 3-3 and 3-7.](image-url)
Because of the high efficiency and unambiguous living chain-growth mechanism of the polymerization, we suggested that this method could be employed to prepare “core-shell” nanoparticles as depicted in Figure 3.1.

First, we prepared a PDCI-incorporating bis-bromide 3-1 to be used as a two-site catalytic “core” (Scheme 3.1). Reaction of 3-1 with 2 equivalents of Ni(dppp)$_2$ in THF at room temperature was monitored by $^{31}$P NMR spectroscopy, which showed complete conversion of 3-1 to bis-Ni(II) catalytic initiator 3-2 in approximately 3 h (Figure 3.2).

![Figure 3.2](image)

Figure 3.2. $^{31}$P NMR of catalytic initiator 3-2 in THF (asterisk represents signal from dppp oxide).

To check if both Ni(II) catalytic sites of 3-2 could independently react in Kumada coupling conditions and that no potential complications (e.g. formation of a reactive/polymerizable radical anion via one-electron reduction as recently described by Senkovskyy et al.$^{30,31}$) could affect the reaction course, we treated 2 with excess 2-thienylmagnesium chloride (Scheme 3.1). The reaction proceeded smoothly and furnished exclusively bis-terthiophene compound 3-3 – the
expected product of Kumada coupling at both Ni(II) reactive sites. In the next step, we checked if 3-2 could act as an external catalytic initiator for polymerization of 5-bromo-4-hexyl-2-thienylmagnesium chloride 3-4. In this case, good solubility of the product polymer 3-7 in the reaction solvent (due to the presence of solubilizing hexyl groups) would preclude formation of insoluble nanoparticles, and therefore would allow structural analysis of the “two-armed” soluble polymer 3-7 by NMR spectroscopy. Reaction of 1 mol % of 3-2 with a solution of 3-4 in THF followed by quenching with 5 M HCl furnished regioregular polymer 3-7 ($M_n$ 12.5 kDa, $M_w/M_n$ 1.06 by GPC). Both the high regioregularity (more than 90%) and low polydispersity index of 3-7 were consistent with living chain-growth polymerization mechanism.  

$^{1}$H NMR spectrum of 3-7 showed PDCI signals in the 8.3-8.9 ppm region which unambiguously proved incorporation of the PDCI “core” in the polymer (Figure 3.3).

Figure 3.3. $^{1}$H NMR of 3-7 in CDCl$_3$. Inset of downfield region in $^{1}$H NMR highlights the aromatic protons associated with the PDCI unit.
Molecular weight of 3-7 estimated from integration of these signals \( (M_n(\text{NMR}) \sim 12 \text{kDa}) \) was in a good agreement with molecular weight obtained from the GPC analysis thus indicating completeness of incorporation of the PDCI “core” within the polymer 3-7 backbone.

With the results of this preliminary investigation pointing on the strong possibility to carry out KCTP with the bi-functional catalytic initiator 3-2, we proceeded to prepare “core-shell” nanoparticles. In order to investigate the effect of a CP “shell” on photoexcitation energy transfer to the low energy gap PDCI “core”, we chose to prepare two kinds of nanoparticles – polythiophene (PDCI-PT) and poly-\( p \)-phenylene (PDCI-PPP) nanoparticles (Scheme 3.1).

![TEM images of PDCI(1.0)-PT (A), PDCI(1.0)-PPP (B), PDCI(0.1)-PPP (C), and PDCI(3.0)-PT (D) nanoparticles. Images C and D were obtained by cryo-TEM in THF solutions, and also show parts of the TEM carbon grid.](image)

Addition of the catalytic initiator 3-2 (1 mol %) to solutions of the Grignard monomers 3-5 or 3-6 in THF resulted in the reaction mixture becoming cloudy within 1-2 min with subsequent formation of a polymer precipitate. The reaction mixture was quenched with 5 M HCl, and the dark precipitate was separated by centrifugation, thoroughly washed with methanol, and dried \textit{in vacuo}. A small amount of the precipitate was suspended in chloroform upon ultrasonication, and
filtered through a 200 nm syringe filter to produce a stable colloidal solution of the nanoparticles. TEM studies of the solution revealed that it contained spherical nanoparticles with an average size of 72 ± 19 nm for PDCI-PT and 78 ± 20 nm for PDCI-PPP nanoparticles (Figure 3.4A-B). The colloidal solutions in chloroform were indefinitely stable and the particles did not disintegrate even after prolonged ultrasonication thus demonstrating their high structural stability.

A support for the proposed living chain-growth polymerization mechanism of nanoparticle formation was obtained via study of the surface composition of the nanoparticles using X-ray photoelectron spectroscopy (XPS), which is a reliable and highly sensitive method to analyze elementary composition of various surfaces. Since nanoparticles were produced through collapsing the polymer “arms” formed via chain-growth polymerization, the polymer end groups remaining at (or near) the particle surface could be detected by XPS. Previously, we have demonstrated that polythiophenes prepared using an externally initiated polymerization approach, similar to the one used in this study, were predominantly terminated with the halogen from the Grignard monomer.29 XPS analysis of nanoparticle samples prepared by drop-casting from the chloroform suspensions showed noticeable signals from halogen atoms: Br for PDCI-PT and both Br and I (in approximately 4 to 1 atomic ratio) – for PDCI-PPP nanoparticles (Figure 3.5). Simultaneous presence of surface Br and I in PDCI-PPP nanoparticles reflected the in situ preparation of Grignard monomer 3-6 by the reaction of 1-bromo-4-iodobenzene with i-PrMgCl which likely made both kinds of halogens available as chain-terminating groups. The presence of XPS-detectable halogen atoms on the surface of the nanoparticles indicated that the nanoparticles were indeed formed via collapsing of the growing polymer “arms” in living KCTP process.
Figure 3.5. Fragments of high-resolution X-ray photoelectron spectra of PDCI(1.0)-PPP (A) and PDCI(1.0)-PT (B) nanoparticles on glass support. The plot displays the areas for Br 3d and I 4d signals. Deconvolution of the signals on spin-orbit split components Br 3d_{3/2} and I 4d_{3/2} (green) and Br 3d_{5/2} and I 4d_{5/2} (blue) is also shown (see Table 6.1 for parameters). Red lines represent simulated spectra, and black lines – experimental data. Atomic % ratio between Br and I in PDCI(1.0)-PPP nanoparticles (as determined from data in graph A) is 82% Br to 18% I.

The relatively uniform size distribution of the nanoparticles reflected the living chain-growth polymerization mechanism responsible for the nanoparticle formation. Furthermore, allowing the polymerization reaction to occur for different amounts of time before quenching with 5 M HCl (ranging from 1 to 60 min) did not noticeably affect the nanoparticle size (Figure 3.6). However, the obtained nanoparticles were of much larger size than expected for the employed ratio of PDCI initiator 3-2 to Grignard monomers, given the presumably single-initiator molecule nature of each nanoparticle. Thus, it was more likely that each nanoparticle consisted of more than one PDCI “core” incorporated during the nanoparticle growth. We further investigated the effect of the initial ratio of catalytic initiator 3-2 to Grignard monomers. The resulting nanoparticles (designated PDCI(X.X)-PT and PDCI(X.X)-PPP, where X.X stands for the mol % fraction of PDCI initiator 3-2 taken for polymerization when keeping the concentration of monomers 3-5 or 3-6 constant) showed strong dependence on this ratio (Figure 3.4C-D).
Figure 3.6. TEM images of PDCI(3.0)-PT nanoparticles obtained using different polymerization time (time between adding the PDCI catalytic initiator 3-2 to Grignard monomer 3-5 solution and quenching the reaction mixture with 5 M HCl).

Much smaller size nanoparticles (around 20 nm diameter) were obtained with 0.1 mol % of 3-2, whereas using 3 mol % of 3-2 yielded a bulk polymer precipitate consisting mostly of very large (400-600 nm) particles which was difficult to suspend upon ultrasonication in chloroform, and the resulting chloroform suspension produced, after filtration through a 200 nm syringe filter, a small yield of large-diameter (~100-150 nm) PDCI(3.0)-PT nanoparticles. Thus, increasing the molar ratio of initiator 3-2 to Grignard monomers presumably lead to larger diameter nanoparticles, with higher fraction of the PDCI “cores”. One of the potential mechanisms for multi-PDCI nanoparticle formation includes pre-aggregation/stacking of the PDCI initiator 3-2 molecules prior to polymerization (in such a case the actual polymerization initiator would behave like a supramolecular aggregate with multiple Ni initiating sites), and would result in a more or less well-defined central “core” in the nanoparticles. As PDCI pre-aggregation would
be more pronounced at higher PDCI concentrations, larger sized nanoparticles obtained with 3 mol % of 3-2 would be more likely to originate from this mechanism. Indeed, some TEM images obtained from CHCl₃ suspensions of PDCI(3.0)-PT nanoparticles clearly displayed well-defined “cores” (Figure 3.7).

![Figure 3.7. Selected TEM images of PDCI(3.0)-PT nanoparticles showing well-defined central “cores”](image)

Presumably, precipitation of the nanoparticles happened before complete consumption of the Grignard monomer 3-5 (or 3-6 for PDCI-PP nanoparticles), and therefore the size of the CP “arms” (and therefore the resulting NP size) was not controlled by the initial ratio of PDCI initiator 3-2 to Grignard monomer. Formation of the larger-size particles obtained with 3 mol % of 3-2 consumed more Grignard monomer which resulted in a higher total yield of the bulk NP precipitate as compared to the formation of the smaller-size nanoparticles with 0.1 mol % of PDCI initiator (e.g. the yield of NP precipitate (based on the amount of Grignard monomer 3-5) was 70% for PDCI(3.0)-PT but only 32% for PDCI(0.1)-PT nanoparticles). An alternative mechanism could involve aggregation of low molecular weight “two-armed” PDCI-conjugated oligomers formed at initial stages of the polymerization, with subsequent growth of the CP branches from the aggregate followed at some point by nanoparticle precipitation. Whereas the first mechanism would likely produce real “core-shell” nanoparticles, the second mechanism
would result in some distribution of PDCI units within the conjugated polymer nanoparticle body (like raisins in a raisin bread). It is also possible that the actual nanoparticle formation could involve combination of both mechanisms. Further research is needed to completely evaluate the structure of the resulting nanoparticles and the mechanisms of their formation.

Since majority of applications of conjugated polymer nanoparticles require them being used in an aqueous (rather than organic solvent) environment, we prepared solutions of both PT and PPP nanoparticles in water.

Figure 3.8. Change in fluorescence spectra of aqueous suspensions of PDCI(3.0)-PT (A) and PDCI(3.0)-PPP (B) nanoparticles (with optical absorbance of ~0.2 a.u.) during storage at room temperature during 7 days. Plot C shows relative integrated intensity of the spectra in A and B (i.e. integrated intensity at each particular storage time normalized by integrated intensity of the as prepared samples). Straight lines correspond to linear fits of the data.

To achieve this, we used a conventional solvent replacement strategy.\textsuperscript{6} Thus, we first suspended a polymer precipitate in THF – a water-miscible solvent – following the same procedure as
described above for the preparation of NP solutions in chloroform. Then, the THF solution was injected in water followed by evaporation of THF on a rotary evaporator. Finally, the resulting aqueous solution was filtered through a 200 nm syringe filter. The aqueous solutions of PDCI-PT and PDCI-PPP nanoparticles were found stable and did not show signs of aggregation or precipitation at least for a few weeks, even despite the absence of specially added stabilizing surfactants (Figure 3.8).

![Fluorescence spectra](image)

Figure 3.9. Change in fluorescence spectra of aqueous suspensions of PDCI(3.0)-PT (A) and PDCI(3.0)-PPP (B) nanoparticles (with optical absorbance of approx. 0.2 a.u.) upon irradiation with 1 mW cm\(^{-2}\) monochromatic light (at 340 nm for PDCI(3.0)-PT and 310 nm for PDCI(3.0)-PPP nanoparticles). Plot C shows relative integrated intensity of the spectra in A and B (i.e. integrated intensity at each irradiation time normalized by integrated intensity of the samples before irradiation).

The high stability of the nanoparticle colloidal solutions could be attributed to the formation of charged surface defect sites due to the CP oxidation during polymerization, as was previously
suggested for explanation of Pdot stabilization.\textsuperscript{32} The nanoparticles also showed high photostability, both in chloroform and in aqueous solutions (Figure 3.9).

UV-vis absorption spectra of the nanoparticle solutions showed broad bands with an onset at around 750 nm (Figure 3.10A). The featureless absorption band with a maximum at \(-600\) nm likely originated from the PDCI “core”, and matched the band found in the absorption spectrum of the “core” itself (compound 3-1, Figure 3.11). Even for the small-molecule compound 3-1, this maximum was substantially bathochromically shifted relative to a similar band in the parent PDCI dye without two bithiophene substituents.\textsuperscript{33}

![UV-vis absorption and fluorescence spectra](image)

Figure 3.10. UV-vis absorption (A) and fluorescence (B) spectra of PDCI(1.0)-PT and PDCI(1.0)-PPP nanoparticles (solid traces – CHCl\(_3\) solution, dashed traces – aqueous solution) and solution of polymer 3-7 in CHCl\(_3\). Fluorescence quantum yields: PDCI-PT NPs 0.02 (CHCl\(_3\)), <0.01 (aq.); PDCI-PPP NPs 0.34 (CHCl\(_3\)), <0.01 (aq.).
Figure 3.11. UV-vis absorption and fluorescence spectra of PDCI “core” compound 3-1 in CHCl$_3$.

The large bathochromic shift and the lack of vibronic fine structure of this band both in compound 3-1 and in the CP nanoparticles prompted us to attribute it as a charge transfer band. Despite the complicated nature of the NP spectra, the highest intensity band with a maximum at 360 nm for PDCI-PT and at 305 nm for PDCI-PPP nanoparticles was likely due to the CP “shell” as could be deduced from the expectedly higher energy of this band in the PDCI-PPP nanoparticles. Most remarkably, the position of this band at much lower wavelengths than in typical soluble PT and PPP polymers indicated dramatically disturbed $\pi$-electron conjugation in the CP nanoparticles. Indeed, for the soluble analogue polymer 3-7 we found a maximum of the similar band at 450 nm – a typical value for PT polymers in “good” solvents, and ~90 nm bathochromically shifted relative to the same band in PDCI-PT nanoparticles. This large hypsochromic shift of the CP “shell” absorption band is a unique feature of the nanoparticles prepared by the “core”-initiated chain-growth polymerization. We can only speculate at this point that tight “wrapping” the CP chains around the small-molecule-size central “core” in the process of collapsing the growing polymer to a nanoparticle might force the polymer chains to highly twisted conformations with severely limited $\pi$-electron conjugation.$^6$ One could also
consider, as an alternative explanation, that, due to their low solubility and related premature precipitation, the CP “arms” formed at the PDCI “core” during polymerization were short oligomers rather than polymers, and thus possessed a short conjugation length consistent with the hypsochromically shifted absorption bands. Although, due to the nanoparticles’ insolubility, we cannot directly measure degree of polymerization of the CP “arms”, it could not be low as otherwise, with only up to 3 mol % of PDCI external catalytic initiator 3-2 used in polymerization, we would have obtained very low yield of the NP precipitate. In reality, with 3 mol % of initiator 3-2, the yield of bulk precipitate of PDCI(3.0)-PT nanoparticles was 70%, and the spectroscopic properties of the crude bulk precipitate were similar to the spectra of the filtered solution of PDCI(3.0)-PT nanoparticles. This indicated identical chemical composition of the crude bulk NP precipitate obtained in the polymerization reaction and the nanoparticles obtained by ultrasoninating the precipitate followed by filtration of the resulting solution through a 200 nm syringe filter. Therefore, we should presume that nanoparticles are composed of CP “arms” of substantial chain lengths, and therefore the NP spectroscopic properties are related to high extent of bending and twisting of the CP “arms”. In any case, we will need further studies to offer any more reliable explanation.

Fluorescent spectra of the nanoparticles, acquired at 350 nm (for PDCI-PT) or 315 nm (for PDCI-PPP) excitation, showed two distinct bands originating separately from the “core” and “shell” units (Figure 3.10B and Figure 3.12). Both PDCI-PT and PDCI-PPP NPs displayed an intense band from the PDCI “core” in the near-infrared range 700-850 nm. As in the case of absorption spectra, the PDCI band both in NPs and in the small-molecule compound 3-1 showed large bathochromic shift relative to the parent PDCI compound, likely related to the charge-
transfer character of this band, which is probably responsible for low fluorescence quantum yields of nanoparticles in aqueous solutions (Figure 3.12).

![Fluorescence spectra of PDCI-PT (A) and PDCI-PPP (B) nanoparticles in CHCl₃ (left pane) and aqueous (right pane) suspensions. Spectra were acquired using excitation at 350 nm for PDCI-PT and 315 nm for PDCI-PPP nanoparticles. Fluorescence quantum yields: PDCI(0.1)-PT 0.02 (CHCl₃), 0.01 (H₂O); PDCI(0.1)-PPP 1.00 (CHCl₃), 0.01 (H₂O); PDCI(1.0)-PT 0.01 (both in CHCl₃ and H₂O); PDCI(1.0)-PPP 0.18 (CHCl₃), 0.01 (H₂O); PDCI(3.0)-PT 0.02 (CHCl₃), <0.01 (H₂O); PDCI(3.0)-PPP 0.34 (CHCl₃), <0.01 (H₂O).](image)

Figure 3.12. Fluorescence spectra of PDCI-PT (A) and PDCI-PPP (B) nanoparticles in CHCl₃ (left pane) and aqueous (right pane) suspensions. Spectra were acquired using excitation at 350 nm for PDCI-PT and 315 nm for PDCI-PPP nanoparticles. Fluorescence quantum yields: PDCI(0.1)-PT 0.02 (CHCl₃), 0.01 (H₂O); PDCI(0.1)-PPP 1.00 (CHCl₃), 0.01 (H₂O); PDCI(1.0)-PT 0.01 (both in CHCl₃ and H₂O); PDCI(1.0)-PPP 0.18 (CHCl₃), 0.01 (H₂O); PDCI(3.0)-PT 0.02 (CHCl₃), <0.01 (H₂O); PDCI(3.0)-PPP 0.34 (CHCl₃), <0.01 (H₂O).

Such near-infrared emission is highly desirable for potential fluorescent imaging and sensing applications of the nanoparticles. Another practical advantage is related to broad absorption
spectrum of the nanoparticles which makes possible to excite them anywhere within the entire visible wavelength range to generate the near-infrared emission (Figure 3.13).

![Fluorescence spectra of the PDCI(1.0)-PT nanoparticles obtained using different excitation wavelengths.](image)

Figure 3.13. Fluorescence spectra of the PDCI(1.0)-PT nanoparticles obtained using different excitation wavelengths.

The high relative intensity of the PDCI band in NP spectra contrasted with essential absence of a similar band in the emission spectrum of polymer 3-7. Indeed, absorption spectrum of 3-7 in dilute solution displayed a small band at around 600 nm due to the PDCI chromophore, and a barely noticeable shoulder near the long-wavelength onset in the fluorescence spectrum of 3-7 could be attributed to the PDCI emission (Figure 3.10B). In fact, direct excitation of the PDCI chromophore in 3-7 (at 600 nm) resulted in the fluorescence spectrum displaying a clear emission band with a maximum at ~770 nm, thus proving the presence of the PDCI group (Figure 3.14). The low intensity of this band in the 3-7 emission spectrum reflected the inefficient energy transfer to the PDCI acceptor from the conformationally extended CP “arms” via through-space Förster mechanism. In contrast, tight “wrapping” of the PT (or PPP) “arms”
around the PDCI “core” in the nanoparticles provided perfect conditions for the highly efficient energy transfer to the low-energy “core”.

![Absorption and emission spectra of polymer 3-7 in CHCl₃ solution.](image)

**Figure 3.14.** Absorption (black trace) and emission (blue trace) spectra of polymer 3-7 in CHCl₃ solution. The emission spectrum was acquired upon direct excitation of the PDCI chromophore (the arrow shows position of the excitation).

Comparison of the emission spectra for NPs prepared using different amounts of external initiator 3-2 revealed an increase in the relative intensity of the near-infrared PDCI band for the nanoparticles prepared using 3 mol % of 3-2 (i.e. PDCI(3.0)-PT and PDCI(3.0)-PPP) relative to the nanoparticles prepared with 1 and 0.1 mol % of 3-2 (Figure 3.12). The higher relative intensity of the near-infrared PDCI emission band likely reflected the increasing concentration of the PDCI “core” in the nanoparticles thus making intra-particle energy transfer to the PDCI “core” more efficient.

To further investigate the intra-particle energy transfer, we carried out pump-probe transient absorption spectroscopy measurements on the aqueous solutions of PDCI(3.0)-PT and PDCI(1.0)-PT NPs to determine the corresponding excited-states relaxation dynamics. Figure 3.15 shows representative transient absorption spectra of the PDCI(3.0)-PT NP solution at different time delays after a 350 nm excitation pump pulse.
Figure 3.15. Representative transient-absorption spectra at different time delays of aqueous solutions of PDCI(3.0)-PT (A) and PDCI(1.0)-PT (B) nanoparticles after 350 nm excitation.

A small PT ground-state depletion band was observed at the 325–342 nm range followed by a sharp depletion band centered at 350 nm. An additional band was observed between 357 and 375 nm and is a convolution of ground-state depletion at short time delays and induced excited-state absorption at longer time delays. The time-dependent transient absorption profiles over the wavelength range of 320–380 nm resulted in the corresponding decay spectra with two different lifetimes $t_1 = 404 \pm 21$ ps and $t_2 = 1460 \pm 81$ ps. The shorter lifetime $t_1$ corresponded to radiative decay of the higher-energy PT chromophore to the ground state and was consistent with normally high radiative decay rate of polythiophenes. On the other hand, the longer lifetime $t_2$ could be associated with the energy transfer from the excited higher-energy PT chromophore to the lower-energy PDCI chromophore. This was confirmed by the transient absorption spectroscopy studies of PDCI(1.0)-PT solution (Figure 3.15B). In this case, a relatively sharp
depletion band centered at 350 nm was attributed to depletion of the PT ground-state electronic population. Transient absorption time profiles of the PDCI(1.0)-PT sample (Figure 3.16) displayed a single-exponential fit with a lifetime of $t = 395 \pm 8$ ps corresponding to the radiative decay of the PT chromophore (matching well the $t_1$ lifetime in the PDCI(3.0)-PT case).

![Figure 3.16](image.png)

Figure 3.16. Transient-absorption spectroscopy data. (A) Time profiles at 335 nm (red trace), 350 nm (blue trace), and 365 nm (green trace), and (B) decay spectra obtained by fitting the transient absorption data to double exponential functions for aqueous suspension of PDCI(3.0)-PT nanoparticles. (C) Time profiles at 350 nm (red trace) and 346 nm (blue trace) for aqueous suspension of PDCI(1.0)-PT nanoparticles.

The lower efficiency of the energy transfer to PDCI chromophore in this case likely made the second lifetime practically undetectable. The transient absorption results were in excellent agreement with the corresponding fluorescence data where the relative intensity of the low-energy PDCI fluorescence band was significantly increased in PDCI(3.0)-PT NPs as compared to PDCI(1.0)-PT NPs (vide supra).
To illustrate the dramatic difference between properties of the nanoparticles described herein and the nanoparticles obtained by traditional reprecipitation or miniemulsion methods, we prepared a series of NPs by reprecipitation using THF solutions of regioregular poly(3-hexylthiophene) (P3HT) polymer without PDCI as well as from P3HT solutions mixed with 0.1, 1.0, and 3.0 mol % of PDCI “core” compound 3-1 (designated here as PDCI/P3HT nanoparticles). We also used miniemulsion method to prepare nanoparticles of soluble polymer 3-7. We were successful in preparation of 3-7 NPs by miniemulsion method, and of pure P3HT and P3HT with 0.1 mol % PDCI nanoparticles by reprecipitation, however, attempts to prepare NPs using 1 mol % of 3-1 resulted in poor quality NPs, and we were unsuccessful in preparation of P3HT nanoparticles with 3 mol % of 3-1. The P3HT nanoparticles showed bathochromically shifted and broadened absorption and fluorescence spectra typical of highly regioregular P3HT films. The area where a PDCI band would be positioned in the absorption spectra was completely covered by the P3HT band, and no distinct PDCI emission band could be found in the fluorescence spectra due to broadening of the P3HT emission. Even if intra-particle excitation energy transfer from P3HT to PDCI chromophores did occur in P3HT nanoparticles, it was not highly efficient and did not result in a strong distinct PDCI emission band, which was observed in the NPs described herein. Overall, these experiments additionally emphasized unique nature and characteristics of the NPs prepared by the “core”-initiated chain-growth polymerization.

3.3. Conclusions

In conclusion, we described the first example of preparation of conjugated polymer nanoparticles by using externally-initiated living chain-growth Kumada catalyst-transfer polymerization with a chromophore “core” external catalytic initiator. The obtained
nanoparticles showed uniform size distribution and high structural stability, in both organic solvent and aqueous solutions, and exhibited dual-band fluorescent emission originating from the “core” and “shell” subunits, with the intense near-infrared “core” emission being due to the efficient intra-particle energy transfer from the “shell” chromophore. Further studies, particularly on how the growing polymer systems in solution collapse to the nanoparticles, more accurate knowledge of the structure of NPs, and ways to control NP size, are required. Nevertheless, the synthetic versatility of this approach and its compatibility with many functional groups opens a way to deliver complex nanoparticle architectures with specific functionalities and tunable spectroscopic properties.

3.4. References


CHAPTER 4. SUPRAMOLECULAR ORGANIZATION AND PHOTOPHYSICAL PROPERTIES OF STIMULI-RESPONSIVE FLUORESCENT AMPHIPHILIC POLYTHIOPHENE COPOLYMERS

4.1. Introduction

In recent years there has been an increasing number of applications that conjugated polymer (CP) materials can be potentially used for, such as photovoltaic cells, organic-light emitting diodes (OLEDs), chemical sensory devices, thin-film transistors, etc.\textsuperscript{1-7} With a growing interest toward CPs in the scientific community and breadth of application comes the necessity to develop a deep mechanistic understanding of excitonic energy transfer within these materials. This fundamental understanding is crucial for the design of next-generation devices, which requires the ability to control structure and supramolecular organization within the molecules themselves.\textsuperscript{8} Pre-organization in solution has been previously shown to dictate macromolecular structure in solid-state, demonstrating the importance of molecular design through structural modification.\textsuperscript{9}

While polythiophenes (PTs) have emerged as an important class of CPs, the mechanism of how exciton migration occurs within a single polymer chain is still debatable.\textsuperscript{10-16} With this in mind, we set out to design a system where we could study the contributions of Dexter and Förster energy transfer in isolated chains through observation of photophysical properties during reorganization in solution and solid-state upon application of an external stimulus. PTs are an ideal candidate to study nanoscale morphology and its effect on optical properties due to PTs conformational changes that can occur upon applying external stimulus.\textsuperscript{17-20} With the important contributions from the McCullough group, synthesis of regioregular PTs (rrPTs) with controlled molecular weight, low polydispersity, and high regioregularity has given a much more
comprehensive insight into morphology and orientation of polymers as important factors into their semiconducting properties.\textsuperscript{21}

Recent work performed by the groups of Kiriy\textsuperscript{22} and Luscombe\textsuperscript{23} have taken the Kumada polycondensation made popular by McCullough\textsuperscript{24} and Yokozawa\textsuperscript{25} and developed the method of external initiation where the initiating species of the living polymerization is incorporated into the end-group of the growing chain. With this in mind, we recently developed a system of direct external initiation, incorporating a functional group into the conjugated chain with unprecedented molecular weights, low polydispersity, and 100\% regioregularity.\textsuperscript{26} This highly efficient system led us to the design of a complex conjugated system based on higher energy stimuli responsive amphiphilic polythiophenes incorporating a low energy central unit.

Water-soluble PTs derivatives have shown to be a strategic method to altering the photophysical properties by controlling organization and structure in solution.\textsuperscript{27} The ability to functionalize PTs accordingly, which allows for solubility in water, poses a large problem for most polymerization techniques since more traditional methods of regioregular polythiophene syntheses do not tolerate aqueous conditions. Post-polymerization functionalization would allow using Grignard metathesis (GRIM) polymerization to synthesize the conjugated backbone in a highly regioregular and well-controlled manner. Subsequently, we could modify the regioregular PT at the 3-position of the thiophene unit followed by atom-transfer radical polymerization resulting in a water-soluble poly(N-isopropylacrylamide) (PNIPAm) polymer branches that are grafted from the backbone of the rigid conjugated polymer chain following similar procedures that had been previously published.\textsuperscript{19} These hydrophilic grafted PNIPAm chains act as both the solubilizing functionalities as well as giving the polymer its stimuli responsive nature. We also expect that the long grafted hydrophilic chains would both insulate
the conjugated backbone as well as increase the propensity for extended macromolecular organization.

In order to monitor the exciton migration through single delocalized chains insulated from other chains we must have a simple mechanism, which would allow reliable assessment of the energy migration within the system. We chose to use a low energy gap central unit so that exciton migration could be monitored by fluorescence spectroscopy. As such a low-energy gap unit, we chose to use a highly fluorescent perylenedicarboximide (PDCI)\textsuperscript{28-30} which could allow for excitons to easily move downhill in energy. The funneling of energy towards the highly fluorescent dye would be easily seen by fluorescence spectroscopy and therefore could allow us to understand greater details on exciton migration within a single CP chain.

We hypothesized that due to the amphiphilicity of the PT molecule, introducing media with varying degrees of polarity would have a large effect on the supramolecular organization and extended network in solution. This preorganization in solution would alter the spectroscopic properties by either 1) planarization/twisting of the conjugated backbone or 2) organization of individual chains into disordered/ordered supramolecular polymer structures which in turn would cause a hypso-/bathochromic shift in absorption spectra. This can be attributed to the localization or extended delocalization of π-electrons within the PT chain. Likewise, as the PNIPAm chains are also temperature-responsive with an LCST ~32°C,\textsuperscript{31-33} we can also apply temperature as an external stimulus in order to induce conformational and organizational changes of the conjugated backbone when the extended hydrophilic PNIPAm chains collapse into a globular state (Figure 4.1).
The presence of PDCI unit that acts as an exciton acceptor would cause a dual-band fluorescence depending on the extent of delocalization. By inducing a conformational change, we can control organization of PTs by pre-forming supramolecular preorganization, which can potentially result in a fluorescent ratiometric response (in both solution and solid state) upon applying an external stimulus.

We herein discuss our approach to synthesize dual-band fluorescent amphiphilic conjugated PTs incorporating a low energy central core unit. Through careful synthetic planning, we can successfully prepare high molecular weight polymers with high regioregularity, low polydispersity, and structurally well-defined blocks containing hydrophilic grafted side-chains. By manipulating the polymer using an external stimulus we can study the organization and mechanisms for energy migration of PTs in both solution and solid-state.

4.2. Results and Discussion


Proper selection of the polymerization initiating species was considered, as our primary target was a low-energy acceptor and fluorescent central core unit. For this reason we chose a
PDCI unit since it is a highly fluorescent electron-poor dye that is photochemically and thermally stable.\textsuperscript{28-30} The details of the synthesis of PDCI polymerization precursor 4-4 was discussed in Chapter 3. Once the dibromide precursor 4-4 was obtained, it was simply treated with 3 equivalents of Ni(dppp)\textsubscript{2} (where dppp = 1,3-bis(diphenylphosphino)propane) at room temperature in order to have complete conversion of 4-4 into the two-armed reactive catalyst 4-5 (Scheme 4.1).

![Chemical diagram](image)

Scheme 4.1. Synthesis of catalytic initiators 4-5 and 4-6.

The conversion of 4-4 to 4-5 could be monitored by \textsuperscript{31}P NMR as explained in Chapters 2 and 3 in this dissertation. It was also important to use a bithiophene catalytic initiator 4-6 as a control
non-PDCI initiator for comparative purposes. The catalytic initiator was used to initiate the controlled Kumada chain-growth process once the respective monomers 4-7 and 4-8 are added. Once all monomer is consumed the polymer can either be a) terminated or b) allowed to further polymerize a growing chain with the addition of more monomer. In this case, we added either monomer 4-7/4-8 first, followed by 4-8/4-7 depending on the targeted polymer obtained which resulted in polymers 4-10 and 4-13, respectively (Scheme 4.2). Likewise, we could simply quench the polymerization reaction with MeOH after addition of monomer 4-7, to obtain 4-9. The non-PDCI block copolymer 4-14 was also synthesized in similar fashion starting with external catalytic initiator 4-6. Polymers 4-10–4-14 could then be easily converted into their respective macroinitiators by careful deprotection in dilute THF upon addition of 2-bromoisobutyryl bromide, giving polymers 4-15–4-19. The macroinitiators 4-15–4-19 were used for subsequent atom transfer radical polymerization (ATRP) of N-isopropylacrylamide resulting in the PNIPAm grafted side-chains (Scheme 4.3). The final amphiphilic copolymers 4-20–4-24 (Scheme 4.3) could be isolated by reprecipitation and purification by column chromatography (see Chapter 6 for more details). The amphiphilic copolymers were soluble in a variety of organic media as well as water.

\(^1\)H NMR spectroscopy and GPC were used in order to fully characterize the prepared conjugated polythiophenes. The controlled character of the polymerization was reflected in polydispersity index (PDI). Interestingly, the \(M_n\)’s of polymers 4-20 and 4-23 are twice that of 4-24, which is a clear indicator that there were two initiating sites on 4-5 as opposed to the single initiating site on 4-6. \(^1\)H NMR also could show the ratios of n:m monomers within a polythiophene backbone. Ratios vary slightly but are all close to 1:1 as would be expected from the ratios of monomers 4-8/4-7 used for polymerization.
Scheme 4.2. Direct externally initiated polythiophene polymer 4-9 and copolymers 4-10–4-14.
Scheme 4.3. Synthesis of macroinitiator 4-15 and subsequent conversion into amphiphilic polythiophene copolymer 4-20. Copolymers 4-16–4-19 and 4-21–4-24 were synthesized following identical protocol to block copolymers 4-15 and 4-20, respectively.
In order to determine if 4-10 and 4-13 are in fact block copolymers and not statistical copolymers, we proceeded to synthesize a statistical copolymer 4-11 by simply polymerizing a mixture of 4-7 and 4-8 in a one-pot process with initiator 4-5. $^1$H NMR spectrum indicates that while block copolymers 4-10 and 4-13 display two distinctive downfield singlets attributed to the thiophene protons in the repeating units of each block, a statistical polymer 4-11 shows a complex downfield signal consisting of a number of peaks almost indistinguishable as individual singlets.

Figure 4.2. Aromatic region in $^1$H NMR of block copolymer precursor 4-10 and statistical copolymer precursor 4-11 in CDCl$_3$.

Furthermore, a deuterated version of block copolymer 4-10 was also synthesized in order to perform neutron scattering experiments discussed in a later section. The polymer 4-12 has its P3HT block deuterated on the hexyl $d$-13 solubilizing alkyl chain.$^{34}$ A summary of
polythiophene backbone polymers as well as amphiphilic grafted polythiophene copolymers is given in Table 4.1.

Table 4.1. Characterization of polythiophene copolymers and their respective PNIPAm-grafted amphiphilic copolymers.

<table>
<thead>
<tr>
<th>Polymer Precursor</th>
<th>$M_n$ (GPC), kDa $^a$</th>
<th>$M_w/M_n$ $^b$</th>
<th>Block Ratio $^c$ (n:m)</th>
<th>%HT $^d$</th>
<th>Polymer</th>
<th>$M_n$ (GPC), kDa $^e$</th>
<th>$M_w/M_n$ $^b$</th>
<th>$\varepsilon_{\text{max}}$</th>
<th>$\Phi$ (PL), soln $^f$</th>
</tr>
</thead>
<tbody>
<tr>
<td>4-9</td>
<td>12.5</td>
<td>1.06</td>
<td>–</td>
<td>100%</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>5.2 x 10^8</td>
</tr>
<tr>
<td>4-10</td>
<td>13.5</td>
<td>1.32</td>
<td>1.7 : 1</td>
<td>100%</td>
<td>4-20</td>
<td>165</td>
<td>1.01</td>
<td>3.96 x 10^8</td>
<td>0.29</td>
</tr>
<tr>
<td>4-11</td>
<td>29.3</td>
<td>1.25</td>
<td>1.2 : 1</td>
<td>100%</td>
<td>4-21</td>
<td>227</td>
<td>1.06</td>
<td>4.31 x 10^8</td>
<td>0.30</td>
</tr>
<tr>
<td>4-12</td>
<td>13.5</td>
<td>1.54</td>
<td>–</td>
<td>–</td>
<td>4-22</td>
<td>133</td>
<td>1.02</td>
<td>2.66 x 10^8</td>
<td>0.31</td>
</tr>
<tr>
<td>4-13</td>
<td>15.1</td>
<td>1.17</td>
<td>1.3 : 1</td>
<td>100%</td>
<td>4-23</td>
<td>163</td>
<td>1.03</td>
<td>3.47 x 10^8</td>
<td>0.36</td>
</tr>
<tr>
<td>4-14</td>
<td>23.2</td>
<td>1.58</td>
<td>1.5 : 1</td>
<td>100%</td>
<td>4-24</td>
<td>89</td>
<td>1.08</td>
<td>2.35 x 10^8</td>
<td>0.36</td>
</tr>
</tbody>
</table>

$^a$ Determined by GPC in THF relative to polystyrene (PS) standards, $^b$ Polydispersity index (PDI, $M_w/M_n$), $^c$ Determined by $^1$H NMR (P3HT vs. P3OTBDMS segment), $^d$ Head-to-Tail, % regioregularity, $^e$ Determined by GPC in THF using a multi-angle light scattering detector (632.8 nm), $dn/dc$: 0.107 mL/g, $^f$ Determined in dilute chloroform solutions ~0.1 mg/mL.

4.2.2. Solvatochromism Studies of Amphiphilic Copolymers.

The spectroscopic properties of amphiphilic block copolymers were investigated upon varying solvent polarity of prepared solutions. It was quickly observed that there was a pronounced solvatochromic effect when dissolving polymers in “selective” methanol and “non-selective” chloroform. While the change in color can be clearly seen visually, they were examined by UV-vis and fluorescence spectroscopy. From the UV-vis spectroscopy we can clearly see a bathochromic shift in the absorption maximum when transitioning from relatively non-polar solvent chloroform to the highly polar solvent methanol (Figure 4.3). When looking at 4-20, 4-23 and 4-24, we can see the absorption maximum ($\lambda_{\text{max}}$) is approximately 440-450 nm in pure “non-selective” chloroform.
Figure 4.3. UV-vis spectroscopy upon varying ratio of CHCl₃ to CH₃OH of block copolymers 4-20, 4-23, 4-24, and statistical copolymer 4-21 in solution. Concentration – 0.07 mg/mL.

Alternatively, when the polymers are dissolved in pure “selective” methanol, the λ_max shifts to ~550-565 nm. The 100 nm shift is also accompanied by a well-defined isosbestic point at approximately 475 nm; this is a clear indicator that there exist two interconverting species in solution rather than a slow transition from one species to another. Fine vibronic structures of the absorption bands in methanol are associated with the supramolecular organization and close-stacking of polymer chains typical of thin-films.⁴⁻³⁵ In the case of statistical copolymer 4-21, changing the ratio of “selective” and “non-selective” solvent showed lack of the molecular organization typical for block copolymers as is apparent by the disappearance of the vibronic features in the absorption bands. It should also be noted that polymer 4-21 shows no well-defined isosbestic point as is the case with the block copolymers, which may indicate the already
disrupted conjugated backbone due to the statistical nature of alternating bulky PNIPAm-grafted side-chains. Solvent-dependent fluorescence spectra were also acquired by excitation at the corresponding isosbestic point (Figure 4.4).

Figure 4.4. Fluorescence spectroscopy upon varying ratio of CHCl₃ to CH₃OH of block copolymers 4-20, 4-23, 4-24, and statistical copolymer 4-21. Concentration – 0.07 mg/mL.

Again, in the cases of amphiphilic block copolymers, we observe decrease in fluorescence ($\lambda_{\text{max}}$ = ~575 nm) upon increasing fraction of “selective” solvent methanol. The block copolymers 4-20 and 4-23 show a gradual decrease whereas block copolymer 4-24 displays a very quick decrease of fluorescence at small fractions of CH₃OH. The statistical copolymer 4-21 is somewhat different in that it shows diminishing fluorescence intensity upon increasing the concentration of CH₃OH, but also shows a clear shift in the $\lambda_{\text{max}}$ from 575 nm to 620 nm. The
observed changes in absorption and fluorescence spectra of amphiphilic copolymers is most likely due to the distinct supramolecular organization that occurs in “selective” solvent. This organization would be the effect of solvating hydrophilic PNIPAm chains. In the case of “non-selective” chloroform, we see a hypsochromic shift due to the lack of solvation of the PNIPAm and an increase in fluorescence quantum yield as the \( \pi \)-electrons become much more localized and would not suffer from excitonic recombination which occurs more frequently in supramolecularly organized polythiophene chains.


While we have explored the solvatochromic properties of amphiphilic copolymers, it was important to investigate the possible supramolecular organization of the polymers in \( \text{CHCl}_3 \) and \( \text{CH}_3\text{OH} \) by cryogenic transmission electron microscopy (cryo-TEM). Cryo-TEM allows to observe the morphology of polymers as they exist in solution. The rapid freezing of the solution in liquid ethane would allow visualizing organization in solution, which is important for understanding structure of these supramolecular assemblies. We can clearly see by the TEM images that when varying solvent polarity we see differences in supramolecular organization (Figure 4.5). In “selective” methanol both 4-20 and 4-21 show distinct morphologies. In the case of block copolymer 4-20, we can observe small fibers \(~200\ nm\) in length, while the statistical copolymer 4-21 shows spheres \(~25\ nm\) in diameter. In “non-selective” chloroform the dissolved polymers don’t seem to show any features but rather a homogenous film despite having a small number of \(~15\ nm\) spheres scattered in between. Most likely the polymer chains are well dissolved and possess structural features smaller than that of the resolution of the TEM.
Figure 4.5. Cryo-TEM images of 4-20 (top row) and 4-21 (bottom row) in “non-selective” chloroform (left) and “selective” methanol (right) with 0.1 mg/mL concentration.

Cryo-TEM images obtained in aqueous solution demonstrate further differences between polymer supramolecular assemblies (Figure 4.6). It is interesting to note the extended network of interpenetrating spheres (~25 nm) for the polymer 4-20 in water. 4-21 exhibits no extended network but shows the larger aggregates with striations that may be a consequence of the particular molecular organization. While we can see that there is some distinct solvent-dependent supramolecular organization in solution, it remains to be explained as to the
morphology and organization at the level of individual chains. For this reason, we undertook neutron scattering experiments which are discussed in a future section.

Figure 4.6. Cryo-TEM images of 4-20 (left) and 4-21 (right) prepared from aqueous solutions with 0.1 mg/mL concentration.

4.2.4. Thermochromic Properties of Amphiphilic Copolymers.

Amphiphilic copolymers also showed noticeable spectroscopic changes upon applying temperature as an external stimulus. As stated previously, PNIPAm branches were chosen as solubilizing groups, enabling the PT chain to become soluble in hydrophilic solvent such as water. PNIPAm in aqueous solutions has also been shown to possess unique thermal characteristics. At lower temperatures PNIPAm chains are extended through hydrogen-bonded solvation, but when heated above the lower-critical solution temperature (LCST) at ~32 °C, the extended chains de-solvate causing a collapse of the extended chains to form globular aggregates. When attached to the thiophene units, this collapse causes twisting of the conjugated polymer backbone, disrupting the delocalization of π-electrons.

Optical spectra were acquired in solution and in spin-cast films of amphiphilic polymers prepared from chloroform, methanol, and water. In all cases, the temperature was varied and
spectral changes were monitored by UV-vis and fluorescence spectroscopy. All the samples showed reversible change upon heating and cooling cycles, and highly reproducible behavior.

Figure 4.7. Variable-temperature, UV-vis (left) and fluorescence (right) spectra of block copolymers 4-20, 4-23, 4-24, and statistical copolymer 4-21 in CHCl₃ solutions (~0.07 mg/mL).

UV-vis spectroscopy of solutions of all polymers in chloroform show very similar changes in which the intensity of the band with λₛₐₜ at approximately 450 nm decreases which is
accompanied by a slight hypsochromic shift upon increase in temperature (Figure 4.7). Fluorescence spectra of the same solutions show similar change as the intensity decreases with an increase in temperature. This could be possibly related to de-aggregation of the supramolecular assemblies at higher temperature. It should also be pointed out that 4-21 showed the most significant change in fluorescence intensity as the temperature changed. As PNIPAm-grafted thiophene units are scattered throughout the statistical PT chain it would make sense to have a larger disruption of planarity, while in the block copolymers there is still roughly half of the PT backbone maintaining the planarization of the P3HT block. In addition, statistical copolymer may form less stable supramolecular aggregates, which show more pronounced de-aggregation upon increasing temperature. While inherent thermochromic behavior has been demonstrated to occur in regioregular P3HTs due to conformation strain on the conjugated backbone, these changes are typically only seen at very high temperatures >100 ºC. 

UV-vis spectra of solutions of block copolymers in methanol show similar characteristics to that of chloroform where there is a slight decrease in optical density as well as a small hypsochromic shift (Figure 4.8). However, the statistical copolymer 4-21 shows a much greater change and lack of the strong vibronic bands associated with the block copolymers. Furthermore, it showed a substantial hypsochromic shift (~50 nm) upon changing temperature from 10 to 60 ºC. Fluorescence spectra of statistical copolymer 4-21 showed an almost ratiometric response to temperature change with an isoemissive point at 595 nm. The initially sharp emission becomes broadened as it becomes blue-shifted. The hypsochromic shift of the emission is probably due to significant steric twisting of the conjugated backbone as this would cause the shorter oligothiophene units to localize π-electrons, thus resulting in a higher energy chromophore. It also could be due to more pronounced de-aggregation, as in the case of CHCl₃ solutions.
Figure 4.8. Variable-temperature, UV-vis (left) and fluorescence (right) spectra of block copolymers 4-20, 4-23, 4-24, and statistical copolymer 4-21 in CH$_3$OH solutions (~0.07 mg/mL).

Interestingly, UV-vis spectra of the polymer solutions in water are much different than that of solutions in methanol (Figure 4.9). All three block copolymers 4-20, 4-23, and 4-24 display vibronic bands at longer wavelengths, and also show some scattering at shorter wavelength due
to forming globular aggregates at temperature above LCST. They all display an isosbestic point at ~475-500 nm.

Figure 4.9. Variable-temperature, UV-vis (left) and fluorescence (right) spectra of block copolymers 4-20, 4-23, 4-24, and statistical copolymer 4-21 in aqueous solutions (~0.07 mg/mL).

In contrast, statistical polymer 4-21 shows no clear isosbestic point and seems to display a much greater scattering at shorter wavelength. The fluorescence spectroscopy of aqueous solutions
shows even more sophisticated behavior with a very complex response to temperature in block copolymers 4-20, 4-23, and 4-24. We can see that upon increasing temperature there is a slight increase in fluorescence intensity at the red-shifted shoulder at approximately 600 nm until reaching the LCST. Once the LCST is reached, overall fluorescence is somewhat diminished. Upon further temperature increase, the fluorescence intensity, again, begins to increase but at this point the red-shifted shoulder has almost completely disappeared and the blue-shifted fluorescence band with $\lambda_{\text{max}}$ at approximately 550-565 nm increases significantly. For the statistical copolymer 4-21, fluorescence exhibits a clear isoemissive point at 605 nm, which would make it an excellent candidate for ratiometric fluorescence temperature detection. What is uncertain at this moment is whether or not the red-shifted fluorescent shoulder at 680 nm is distinct PDCI fluorescence band overlapping with polythiophene fluorescence or this is a band resulting from aggregation of PT chains. We can speculate at this point that it could be fluorescence emission as a result of funneling of excitons towards the low-energy central core. As 4-21 is a statistical copolymer with initially lower $\pi$-electron extended delocalization, we can assure that the initial bathochromic shoulder could be fluorescence of the PDCI. This would also demonstrate the disruption in excitonic migration towards the central core as the temperature is increased as we can see a hypsochromic shift of the dominant $\lambda_{\text{max}}$ at 520 nm with a concomitant decrease in emission intensity.

While it is important to look at supramolecular organization and photophysical properties in solution, it is just as important if not more important to be able to observe the same phenomena in solid-state. Similarly to solutions we investigated a series of spun-cast films that were prepared from different solvents such as chloroform, methanol, and water. As the films are
subjected to variable temperature, they show unique response by optical spectroscopy. First, we looked at thin-films prepared from solutions in chloroform (Figure 4.10).

![Figure 4.10](image)

Figure 4.10. Variable-temperature, UV-vis (left) and fluorescence (right) spectra of films of block copolymers 4-20, 4-23, 4-24, and statistical copolymer 4-21 spin-cast from CHCl₃ solutions.

UV-vis spectra of thin films are somewhat different from that of solutions in CHCl₃. The λ_max of spin-cast films 4-20 and 4-23 are blue-shifted relative to that of 4-24. 4-20 and 4-23 have a λ_max
of 560 nm while \textbf{4-24} has similar features to that of block copolymers dissolved in methanol with a $\lambda_{\text{max}}$ of 520 nm and also possesses the vibronically structured bands. While \textbf{4-20} and \textbf{4-23} also display some vibronic features, they are not as pronounced as that of \textbf{4-24}. Statistical copolymer \textbf{4-21}, on the other hand, shows a similar $\lambda_{\text{max}}$ at 450 nm as its block copolymer counterparts \textbf{4-20} and \textbf{4-23}, yet the band is much narrower and lacks any vibronic features. The fluorescence spectra of spin-cast films prepared from chloroform solutions differ when comparing block copolymers \textbf{4-20}, \textbf{4-23}, and \textbf{4-24} with statistical copolymer \textbf{4-21}. In the block copolymers \textbf{4-20} and \textbf{4-23}, the band with $\lambda_{\text{max}}$ at 595 nm increases in intensity with the temperature rise. Similarly, block copolymer \textbf{4-24} shows increase in intensity of the band with $\lambda_{\text{max}}$ 575 nm as temperature is increased. In contrast, statistical copolymer \textbf{4-21} shows band with $\lambda_{\text{max}}$ at 565 nm seemingly decreasing upon increasing temperature – an opposite behavior to that of block copolymers. The films spin-cast spin-cast from methanol solutions show very similar behavior in UV-vis spectra to that of their solution counterparts where we see a slight decrease and hypsochromic shift in absorption (Figure 4.11). What is interesting is that in block copolymer \textbf{4-23} shows almost no change upon heating in methanol solution, while in solid-state it shows a significant decrease in fluorescence intensity. The $\lambda_{\text{max}}$ is also significantly bathochromically shifted compared to that of the methanol solutions. The $\lambda_{\text{max}}$ of the emission band in block copolymer \textbf{4-23} is closer to that of statistical copolymer \textbf{4-21}, although \textbf{4-23} shows almost no change in fluorescence other than a slight hypsochromic shift.

Finally, variable-temperature spectroscopic study of spin-cast films prepared from aqueous solutions shows significant temperature-induced response (Figure 4.12).
Figure 4.11. Variable-temperature, UV-vis (left) and fluorescence (right) spectra of films of block copolymers 4-20, 4-23, 4-24, and statistical copolymer 4-21 spin-cast from CH$_3$OH solutions.

In particular, UV-vis spectra of block copolymers 4-20, 4-23, and 4-24 shows very similar characteristics to the spectra of the same polymers in aqueous solution. Statistical copolymer 4-21, on the other hand, shows a slight hypsochromic shift and what appears to be an almost unnoticeable isosbestic point at 495 nm.
Figure 4.12. Variable-temperature, UV-vis (left) and fluorescence (right) spectra of films of block copolymers 4-20, 4-23, 4-24, and statistical copolymer 4-21 spin-cast from aqueous solutions.

The fluorescence spectra show a much larger dissimilarity between block copolymers containing PDCI versus block copolymer 4-24 which does not contain PDCI. As can be seen in Figure 4.12, non-PDCI block copolymer 4-24 shows almost no change at all, while block copolymers 4-20 and 4-23 show a significant increase in fluorescence. Statistical copolymer 4-21 shows a
slight increase in fluorescence along with a slight hypsochromic shift. It also no longer shows an isoemissive point observed in H₂O solution. In addition, the red-shifted shoulder at approximately λ_max of 675 nm, which we had originally attributed to the strong fluorescence of PDCI central core, did not show intensity decrease found for this polymer in aqueous solution. This may be due to the restricted conformational freedom of the polymer chains in thin film.³⁹ Optical spectra of thin-films prepared from aqueous solutions are in agreement with those of the solutions, demonstrating the importance of the solvent polarity for amphiphilic copolymers. The non-PDCI control polymer showed no spectroscopic response in fluorescent spectra, despite showing a noticeable temperature-induced change in UV-vis absorption spectra (Figure 4.12). This indicates that energy transfer to the lower-gap PDCI unit (and its temperature-induced modulation) play an important role in the spectroscopic properties of the copolymers 4-20–4-23.  

4.2.5. Small-angle Neutron Scattering (SANS) Studies.

Neutron scattering is an attractive tool for the structural characterization of organic materials due to the high scattering cross section for light elements and the ability to tune contrast through isotope labeling. Hydrogen (¹H) and deuterium (²H) have differing cross sections for neutrons so the site-selective deuteration can make some part of the material more visible than the other. Extended q-range small-angle neutron scattering (EQ-SANS) studies were undertaken at the Spallation Neutron Source (SNS) in order to determine morphological structures of polymers⁴⁰ in organic and aqueous media, with the goal to gain better insight into supramolecular organization. Such organization of the copolymers is a crucial factor when processing materials from conjugated polymer solutions as the solution organization and structure will dictate the organization in solid-state. Small-angle scattering of polymer solutions is measured as a function of scattering vector q (momentum transfer) where pulsed sources such as SNS use fixed angles
and variable incident wavelength. We observe intermediate to high q-range in which we can determine statistics of the polymer chain and its persistence length as well as macromolecular organization through various model fitting. This is accomplished by comparison of non-deuterated block copolymer 4-20, deuterated block copolymer 4-22, and non-deuterated statistical copolymer 4-21. SANS data shows big differences on the log \( I(q) \) versus \( q \) plot both at low \( q \), and large \( q \) where different power law behaviors are observed and will be discussed in more details below. It is also important to note that the scattering length densities of both CD\(_3\)OD solvent and the deuterated hexyl (C\(_6\)D\(_6\)) substituent on P3HT in 4-22 have been phase (index) matched (Table 4.2). Furthermore, CDCl\(_3\) is a good solvent for the hydrophobic P3HT block yet not as good for the PNIPAm-grafted polythiophene block. While CD\(_3\)OD is still a decent solvent for the hydrophilic PNIPAm-grafted block, it is marginally worse than that of CDCl\(_3\) for the P3HT block. This solvent selectivity of the two blocks leads to different forms of aggregation behavior in two solvents as observed by SANS measurements described below.

Table 4.2. Summary of calculated scattering length densities (SLDs) for small-angle neutron scattering (SANS) experiments.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Formula</th>
<th>Density (g/mL)</th>
<th>SLD (Å(^{-2})) (^a)</th>
</tr>
</thead>
<tbody>
<tr>
<td>d-Chloroform</td>
<td>CDCl(_3)</td>
<td>1.5</td>
<td>3.16 x 10(^{-6})</td>
</tr>
<tr>
<td>d-Methanol</td>
<td>CD(_3)OD</td>
<td>0.888</td>
<td>5.8 x 10(^{-6})</td>
</tr>
<tr>
<td>d-Water</td>
<td>D(_2)O</td>
<td>1.107</td>
<td>7.26 x 10(^{-6})</td>
</tr>
<tr>
<td>P3HT</td>
<td>C(<em>{10})H(</em>{14})S</td>
<td>1.1</td>
<td>0.68 x 10(^{-6})</td>
</tr>
<tr>
<td>d-P3HT</td>
<td>C(<em>{10})D(</em>{13})S</td>
<td>1.1</td>
<td>5.62 x 10(^{-6})</td>
</tr>
<tr>
<td>PNIPAm</td>
<td>C(<em>{6})H(</em>{11})NO</td>
<td>1.1</td>
<td>8.14 x 10(^{-6})</td>
</tr>
</tbody>
</table>

\(^a\) Determined at 1 Å wavelength.

Copolymers 4-20, 4-21, and 4-22 were all measured in both CDCl\(_3\) and CD\(_3\)OD solutions and plotted as log \( I(q) \) versus \( q \) (Figure 4.13). The solution concentration was 10 mg/mL – this
relatively high concentration was required to obtain detectable signal. In the case of block copolymer 4-20 at high and intermediate \( q \)-range in CDCl\(_3\), we observe a power law regime between \( q \) of 0.28 Å\(^{-1}\) (length scale \( r \approx 22 \) Å) to 0.1 Å\(^{-1}\) (\( r \approx 62.8 \) Å) that displays \( I(q) \sim 1/q \), which could be a result of the high persistence length or rod-like characteristics of the rigid polythiophene backbone in hydrophobic solvent, whereas in a hydrophilic solvent CD\(_3\)OD we observe \( I(q) \sim 1/q^{1.1} \) between \( q \) of 0.28 Å\(^{-1}\) (\( r \approx 22 \) Å) to 0.45 Å\(^{-1}\) (\( r \approx 15.7 \) Å) which shows the polymer interaction in a good solvent for the hydrophilic PNIPAm-grafted polythiophene block. We also observe the \( I(q) \sim 1/q \) behavior in CDCl\(_3\) crosses over to \( I(q) \sim 1/q^2 \) between \( q \) of 0.09 Å\(^{-1}\) (\( r \approx 70 \) Å) to 0.019 Å\(^{-1}\) (\( r \approx 331 \) Å) corresponding to a 2-D random walk in a marginally good solvent. In contrast, the chain statistics of the same block copolymer 4-20 in CD\(_3\)OD exhibits \( I(q) \sim q^{-1.67} \) behavior up to 0.057 Å\(^{-1}\) (\( r \approx 110 \) Å) but then crosses over to \( I(q) \sim 1/q^{3.14} \) between 0.03 Å\(^{-1}\) (\( r \approx 209 \) Å) to 0.016 Å\(^{-1}\) (\( r \approx 390 \) Å) corresponding to the PNIPAm-grafts in a good hydrophilic solvent (self-avoiding walk) and an ambiguous “fuzzy” interface according to Porod’s Law, respectively. Furthermore, the \( I(q) \sim 1/q^{3.14} \) corresponding to 4-20 in CD\(_3\)OD would indicate that it is a 3-D object with fractal interfaces.

At low \( q \), the radius of gyration \( R_g \) can be determined independent of the shape of the object provided we are in the regime \( qR_g \leq 1 \) and there are no interactions at low concentrations (3 mg/mL). In CDCl\(_3\) solution, we are in a regime \( qR_g \approx 1 \) and can accurately determine the \( R_g \) of the block copolymers in the solvent and from the \( R_g \) values calculate a rough characteristic size assuming a spherical object determined as 213 Å, 143 Å, and 82 Å for 4-20, 4-21 and 4-22, respectively. In CD\(_3\)OD solutions, we are in a regime \( qR_g \approx 1 \) and thus we cannot accurately determine the \( R_g \) and the characteristic size of the block copolymer supramolecular aggregates. This is because the size of the object is too big and therefore we have to measure down to much
lower $q$ to determine the $R_g$ accurately. Thus the drawback of this method is that the range of $q$ values at low $q$ where we obtain a linear plot is limited. At higher polymer concentrations, such Guinier analysis is more flawed due to interaction between many chains, which show up at low $q$’s and also due to polydispersity in the size of the objects.

Figure 4.13. Small-angle neutron scattering (SANS) data of copolymers 4-20–4-22 in CDCl$_3$ (“good” solvent) and CD$_3$OD (“bad” solvent) at 10 mg/mL concentration.

An alternative way of analyzing the SANS data is the Kratky plot where $I(q)q^2$ is plotted against $q$. Such an analysis is important as it allows to observe change of power law behavior and determining the crossover from Gaussian (or excluded free volume) behavior to rod-like behavior. Normally, for a pure Gaussian chain the Kratky plot is flat. The maxima in the SANS data can be explained qualitatively by assuming that the polymers exist in more compact structures than linear chains (Figure 4.14). The $q$ at a corresponding maximum in the curve corresponds to characteristic length in the system (proportional to the number of pairs at a
distance $R$ such that $qR=2\pi$). A plot of $q^2I(q)$ versus $q$ exhibits a deviation from the Gaussian chain in the case of both 4-20 and 4-21 in CD$_3$OD while in CDCl$_3$ we observe that the polymers exist in a Gaussian chain at low $q$ and at higher $q$ exhibit rodlike behavior. Similarly, 4-22 exhibits the same behavior in both CDCl$_3$ and CD$_3$OD.

Figure 4.14. Kratky plots of SANS data for copolymers 4-20–4-22 in CDCl$_3$ (“good” solvent) and CD$_3$OD (“bad” solvent) at 10 mg/mL concentration.

Copolymer 4-20 in CD$_3$OD displays a much more statistical probability with an increased intensity at a characteristic size of $\sim 660$ Å, while 4-21 shows a smaller size of $\sim 314$ Å and broader size distribution compared to that of 4-20. The size in CD$_3$OD can be attributed to an extended 3-D structure where planar hydrophobic P3HT blocks may be forming $\pi$-stacked aggregates while large PNIPAm hydrophilic side chains extend outwards into a large network, however, due to the constraints of the $q$-range, this structure may be larger than the given values. The $\sim 224$ Å and $\sim 261$ Å size in CDCl$_3$ of 4-20 and 4-21, respectively, could be roughly the size
of a single cylindrical chain. This would mean that in CDCl₃, polymers show no extended network, yet act as rod-like or cylindrical chains homogenously distributed in solution.

As PNIPAm-grafted chains reach an LCST at ~32 °C in water, it is critical to look at macromolecular structure by SANS at both above (45 °C) and below (15 °C) the LCST in D₂O. A log \( I(q) \) versus \( q \) plot of copolymers in D₂O at 15 °C (Figure 4.15) is very similar to that in CD₃OD at room temperature, yet the \( I(q) \sim q^{-2.5} \) suggests that D₂O may be a slightly worse solvent (random walk) than CD₃OD (also there is more scattering contrast from P3HT than from the PNIPAm-grafted polythiophene block in D₂O). Most importantly is that at lower temperatures at small \( q \) we see that there are rod-like or cylindrical chains that may be isolated. However, once the temperature is above LCST we observe spherical-like global structures as the \( I(q) \) is now greater than 4 (due to curvature corrections to a sharp interface). The Kratky plot (Figure 4.16) further demonstrates this by attributing a size of ~450 Å at low temperature and ~1000 Å at high temperature. Interestingly, we can also see a small correlation peak at ~10 Å in all copolymers in D₂O at 45 °C (Figure 4.15). If this were due to the hexylthiophene portion of the polymer chain, this feature would most likely not be visible for the deuterated P3HT block in D₂O. Therefore, it is possible that this could be a feature of the central PDCI core stacking, however, it may also be attributed to the interchain distance between aligned hexyl substituents in the organized P3HT blocks.

Since it appears that there are well-defined spherical structures at temperature above LCST for the copolymers, the SANS data could be plotted as \( q^4 I(q) \) versus \( q \) (Porod plot) in order to describe shape and size without being affected by intermolecular supramolecular aggregation.
Figure 4.15. Small-angle neutron scattering (SANS) of copolymers 4-20–4-22 in D$_2$O (concentration – 10 mg/mL) at 15 °C and 45 °C, the temperatures below and above the LCST of PNIPAm, respectively.

Figure 4.16. Kratky plots of copolymers 4-20–4-22 in D$_2$O (10 mg/mL) at 15 °C and 45 °C corresponding to being below and above LCST of PNIPAm, respectively.
It is quite apparent that block copolymers 4-20–4-22 exhibit spherical morphologies with a radius of ~30 nm similar to what we see in cryo-TEM image in Figure 4.6 for block copolymer 4-20 in H$_2$O. While it is clear that we have spherical structure with a characteristic radius, the dampening indicates that the copolymers are somewhat polydisperse (~20% shown by a fit to a model of Schultz-Flory distribution$^{41}$ of the polydisperse spheres for 4-20). The contrast from the oscillations is lower especially for the deuterated 4-22 due to its scattering length density being closer to that of D$_2$O (refer to Table 4.2). We are currently in the process of stitching...
together the SANS data to derive a distinct structural picture of the supramolecular assemblies of
amphiphilic copolymers in different solvents.

4.3. Conclusions

We have demonstrated the ability to control morphology and supramolecular organization of
amphiphilic conjugated polymers based on polythiophene block copolymers. Successful
incorporation of the PDCI core into the conjugated polymer backbone enabled the monitoring of
energy migration within isolated PT chains and its temperature-induced modulation. Spectroscopic properties show that changes in organization affect the electronic properties of the
conjugated polymer by disruption of the $\pi$-delocalization as well as by de-aggregation of the
supramolecular structures. Solvatochromic and thermochromic effects are further studied in
small-angle neutron scattering experiments where the supramolecular structure is drastically
changed upon external stimulus (solvent and temperature). The investigation brought light to
supramolecular organization determining exciton migration in conjugated polymer chains.
Further SANS and small-angle X-ray scattering (SAXS) experiments are being undertaken in
order to have a clear understanding of the local and global structures of amphiphilic
polythiophene copolymers in solution and in thin films.

4.4. References

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CHAPTER 5. STEREOSELECTIVE PREPARATION AND PROPERTIES OF cis- AND trans-POLY(p-PHENYLENE ETHYNYLENE VINYLENE)S

5.1. Introduction

Conjugated polymers (CPs) received much attention in recent years due to their interesting semiconducting, optical, and thermal properties.\(^1\)-\(^3\) Ushering in new materials will be an important topic of research as scientists seek to increase the tools used to design future electronic devices. Although this has become an increasing field with numerous disciplines contributing to investigations into next generation materials, there is still room to grow. The synthesis of semiconducting polymers has seen a steady increase in number of useful methods useful in controlled polymerizations, whether that is through traditional polycondensation or chain-growth mechanisms. For example, Bielawski has demonstrated the chain-growth synthesis of poly\((p\text{-phenylene ethynylene})\) (PPP) – a conjugated polymer that is conventionally prepared via step-growth polycondensation. Meanwhile, Yokozawa demonstrated preparation of poly\((p\text{-phenylene vinylene})\) (PPV) by Pd catalyst-transfer mechanism. This, however, comes with significant challenges and downfalls.

While there has been extensive research on synthesis and applications of both PPEs\(^4\)-\(^5\) and PPVs,\(^6\)-\(^7\) there is little existing research on poly\((p\text{-phenylene ethynylene vinylene})\) (PPEV) – a novel class of semiconducting polymers. PPEVs are characterized by their alternating phenylene–C=C–C≡C units. Although investigations of homodimerization of terminal aryl alkynes using transition metal catalysts such as ruthenium, palladium, nickel, etc. have been extensive, little is known about polymers of similar functionality.\(^8\)-\(^10\) Recently, Bassetti was successful in synthesizing low molecular weight oligomers of phenylene ethynylene vinylene, which displayed interesting optical properties comparable to that of high molecular weight PPVs and PPEs.\(^11\)-\(^12\) Exploring potential use for PPEVs may lead to more opportunistic devices as the
band gap should hypothetically lie similar to that of PPVs. This allows for the fine-tuning of optical properties required for applications in optoelectronic devices.

5.2. Results and Discussion

In this work, we present the stereoselective preparation of soluble cis- and trans-PPEVs through the use of Ru(PPh$_3$)$_3$Cl$_2$ or Pd(IPr)$_2$ transition metal catalysts, respectively. The latter Pd catalyst is used with an equimolar amount of the sterically bulky ligand tris(2,6-dimethoxyphenyl)phosphine (TDMPP) while the former Ru complex is used in combination with a novel phosphine ligand pincer complex 5-2. We have found that both catalytic systems perform the tail-to-tail polymerization of terminal aryl acetylenes (Scheme 5.1).

![Scheme 5.1. Synthesis of poly($p$-phenylene ethynylene vinylene)s (PPEVs).](image)

However, further investigation led us to find that 1,1'-bis(diphenylphosphino)ferrocene (dppf) could also be used for cis-selective ene-yne formation when employed as a ligand in tandem with the Ru(PPh$_3$)$_3$Cl$_2$ catalyst. The direct tail-to-tail coupling of terminal acetylenes allows for a facile synthesis of PPEVs without the use of two separate monomers or the need for a hybrid PPE-PPV polymer to accomplish successful bandgap engineering.$^{13-14}$

Synthesis of Pd(IPr)$_2$ carbene complex began with treatment of [(IPR)Pd(allyl)Cl] with KOtBu in iPrOH following previously reported methods.$^{15}$ The Ru(PPh$_3$)$_3$Cl$_2$ could be obtained commercially, however ligand 5-2 had to be synthesized according to the proper procedure in the experimental section of this dissertation. A highly branched alkoxy-substituted phenyl-bis-
acetylene monomer 5-1 was chosen due to the poor solubility of unsubstituted phenyl-bis-acetylenes and could be synthesized following usual approach to similar compounds in literature. While it is known that Pd(IPr)_2 is efficient in tail-to-tail trans-coupling of terminal acetylenes, Ru(PPh_3)_3Cl_2 has not previously been described to couple terminal acetylenes cis-selectively. In order to determine stereoselectivity of the coupling, phenylacetylene was chosen as a model compound for the tail-to-tail Z-coupling (Scheme 5.2).

\[
\begin{align*}
\text{Br} & \quad \text{Br} \\
PPh_2 & \quad PPh_2
\end{align*}
\]

\[
\text{Ru(PPh}_3\text{)_3Cl}_2 \text{ (10 mol\%)}
\]

\[
110 \text{ °C, 24-48 h}
\]

Scheme 5.2. Tail-to-tail coupling of phenylacetylene with Ru(PPh_3)_3Cl_2 and corresponding pincer complex 5-2.

The results of the coupling of 5-3 determined that the catalyst was in fact selective for the Z-isomer after the isolated major product was characterized by ^1H NMR. Interestingly, head-to-tail coupling was not unobserved as well as no E-isomer tail-tail product. This is important for comparison as trace presence of other coupling junctions on the polymer chain would be impossible to separate after polymerization and could potentially affect optical properties of the resulting polymer. As the coupling of two phenylacetylene proved to be successful, polymerization of phenyl-bis-acetylene 5-1 was subsequently undertaken following similar protocol for the homocoupling of 5-3. Similarly, the polymerization was performed in similar fashion using Ru(PPh_3)_3Cl_2, but instead with dppf acting as ligand.
Table 5.1. Characterization of cis- and trans-PPEV polymers and their respective fluorescence quantum yields.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Catalyst</th>
<th>Ligand</th>
<th>Yield %</th>
<th>$M_n$ (GPC)$^a$</th>
<th>$M_w/M_n$$^b$</th>
<th>$\Phi$ (PL), soln$^c$</th>
<th>$\Phi$ (PL), film</th>
<th>$\varepsilon_{\text{max}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>5-4</td>
<td>Ru(PPh$_3$)$_2$Cl$_2$</td>
<td>5-2</td>
<td>6%</td>
<td>6 kDa</td>
<td>1.33</td>
<td>0.21</td>
<td>0.01</td>
<td>11,019</td>
</tr>
<tr>
<td>5-5</td>
<td>Ru(PPh$_3$)$_2$Cl$_2$</td>
<td>dppf</td>
<td>6%</td>
<td>6 kDa</td>
<td>1.43</td>
<td>0.19</td>
<td>0.03</td>
<td>10,625</td>
</tr>
<tr>
<td>5-6</td>
<td>Pd(IPr)$_2$</td>
<td>TDMPP</td>
<td>89%</td>
<td>16 kDa</td>
<td>2.3</td>
<td>0.63</td>
<td>0.16</td>
<td>3,640</td>
</tr>
</tbody>
</table>

$^a$ Determined by GPC in THF relative to polystyrene (PS) standards; $^b$ Polydispersity index (PDI, $M_w/M_n$); $^c$ Dilute chloroform solutions ~20 µM.

Following precipitation of PPVEs, characterization by $^1$H NMR and Gel-Permeation Chromatography (GPC) was undertaken as summarized in Table 5.1. Most notably was the inability to obtain cis-PPEVs 5-4 and 5-5 in high molecular weight, likely due to the sterically crowded alkyl chains which inhibit growth of the polymer chain during the polymerization process, resulting in a relatively low polydispersity index (PDI) of <2.0. In contrast, trans-PPEV was easily prepared with high molecular weight when catalyzed via Pd-carbene complex in the presence of TDMPP ligand. This finding is important as there is little to no cases of high molecular weight ene-yne conjugated polymers prepared using a direct tail-to-tail coupling of terminal alkynes. The polydispersity of PPEV 5-6 is consistent with that of a typical step-growth polymerization indicating that the catalytic center was not associated with a growing polymer chain during polymerization. However, further mechanistic experimentation must be investigated in the near future.

Optical properties were investigated by UV-vis and fluorescence spectroscopy in dilute chloroform solutions and in spin-cast films (Figure 5.1). The importance of the UV-vis spectroscopy provides is that it provides insight into the macromolecular organization of the polymer chains in solution and solid-state.
Figure 5.1. Normalized UV-vis and fluorescence spectra of PPEVs 5-4, 5-5, and 5-6 in ~30 µM chloroform solution (black traces) and spin-cast films (red traces).
When comparing the absorption spectra of the two cis-PPEVs, we found a strong prominent band at ~325 nm in both 5-4 and 5-5 corresponding to the π–π* absorption. However, 5-5 also showed a pronounced red-shifted broad band at 420 nm, which appears only to be a shoulder in 5-4. There may be some possibility of minor trans-C=C units present within the backbone of 5-5, which produced the red-shifted band. This could be confirmed by the presence of multiple peaks observed in the 1H NMR of 5-5 at ~3.7 ppm (see Appendix B). This would indicate the –OCH₂ of the alkoxy groups adjacent to the vinylene units were in different environments. The trace presence of trans-C=C junctions can also be seen in the emission spectra of 5-5 in solution, where the λ_max at ~500 nm was found to be similar to the λ_max of trans-PPEV of 5-6. Alternatively, 5-4 does not show multiple peaks for –OCH₂ protons in 1H NMR yet still has somewhat of a bathochromic shoulder, which may be simply caused by aggregation or be a result of the alkoxy auxochrome. Clearly the hypsochromic nature of the cis-PPEV is consistent with a decrease in the extent of π-conjugation as the backbone which likely assumes a helical structure and suffers from the strong steric repulsion of the bulky side chains in such a structure. In contrast, the red-shifted absorbance and emission spectral bands of the trans-PPEVs would indicate the increased π-delocalization of the conjugated backbone. All three PPEVs 5-4–5-6 display green fluorescent emission with bands lying in between typical alkylated PPE (blue) and PPV (green).

Fluorescence quantum yields for cis-PPEVs were found to be significantly lower than those of the trans-PPEV (Table 5.1), which can also be explained by the increased delocalization in trans-PPEV 5-6. Emission spectra of solid-state spin-cast films are characterized by the significant red-shift of the bands in both cis- and trans-PPEVs. Most notably is the pronounced bimodal distribution of emission when going from solution to solid state in 5-6. This is possibly
due to the ability of high molecular weight linear trans-PPEV to form \( \pi-\pi \) aggregates as the extended conformation allows for the stacking of polymer chains. Optical bandgaps could be calculated from the onset of absorption, which also was in agreement with electrochemical bandgaps described below (Table 5.2).

Table 5.2. Electrochemical and optical bandgaps of PPEV polymers.

| Polymer | Electrochemical Bandgap | Optical Bandgap
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>5-4</td>
<td>2.43 eV</td>
<td>2.31 eV</td>
</tr>
<tr>
<td>5-5</td>
<td>2.39 eV</td>
<td>2.2 eV</td>
</tr>
<tr>
<td>5-6</td>
<td>2.48 eV</td>
<td>2.36 eV</td>
</tr>
</tbody>
</table>

\(^a\) Determined by the onset of absorbance in dilute \(~30\ \text{µM}\) chloroform solutions.

Electrochemical studies were carried out on cis- and trans-PPEVs in order to determine bandgaps (Figure 5.2). Cyclic voltammetry (CV) data were obtained in dichloromethane solutions containing a 0.1 M tetrabutylammonium hexafluorophosphate (Bu\(_4\)NF\(_6\)P). All potentials were measured with respect to ferrocene (Fc). Electrochemical bandgaps were calculated by the difference of onset between oxidation and reduction as reported in Table 5.1. Unfortunately due to the insufficient electrochemical window of the dichloromethane solvent, we were unable to acquire a complete oxidation peak yet still managed to obtain the shoulder. While it would be expected for trans-PPEV to show the theoretically lowest bandgap (compared to cis-PPEVs), this in fact was not the case. Indeed, all the measured electrochemical bandgaps fall within the same range of experimental error. As mentioned earlier, the electrochemical bandgaps were also consistent with the bandgaps obtained from optical absorbance spectroscopy.
Figure 5.2. Cyclic voltammetry data of 5-4, 5-5, and 5-6 in CH$_2$Cl$_2$ containing 0.1 M Bu$_4$NF$_6$P as electrolyte. Scan rate = 100 mV/s with Pt button working electrode (diameter 2 mm).

Thermal stability of PPEVs was measured using thermogravimetric analysis (TGA) under N$_2$. Both cis- and trans-PPEV polymers were found stable up to approximately 365 °C. Soluble conjugated polymers typically show lower thermal stability than that of their unsubstituted counterparts due to the instability originating from forming reactive radicals on the α-carbon of the alkyl side chains.$^{18}$

Variable temperature-dependent absorption and fluorescence spectra of PPEVs in chloroform solutions showed slight intensity decrease without wavelength shift upon increasing temperature (Figure 5.4). At the same time, trans-PPEV 5-6 showed no temperature-induced spectral change. The temperature response could be due to torsional strain of the conjugated backbone or could simply be due to the systematic experimental error as there is not a large change.
Figure 5.3. TGA curves for PPEV polymers 5-4, 5-5, and 5-6.
Figure 5.4. Variable-temperature optical spectra of 5-5 in chloroform.

Similar phenomena have been observed in other conjugated polymers such as poly(3-hexylthiophene) (P3HT).\(^{19}\) Although there is no shift in wavelength, there is a loss of fluorescence, which could be a result of further loss of delocalization of \(\pi\)-electrons, or creating more quenching exciton traps upon temperature increase.

As conjugated polymers are typically brittle and rigid, to our surprise we found that the trans-PPEV 5-6 was a flexible, almost rubbery solid. There has only been one report of “gum-like” conjugated polymers reported where poly(diphenylacetylene)s were functionalized with very long octadecylsilyl groups at either the para- or meta-position.\(^{20}\) To gain better insight into the rubbery characteristics, we used differential scanning calorimetry (DSC) to determine transition properties as a function of temperature. While it is difficult to conclude from the DSC plot in Figure 5.5 about low glass transition temperature (Tg) there does seem to be a clear endothermic process occurring at low temperatures.
Figure 5.5. Differential Scanning Calorimetry (DSC) of *trans*-PPEV 5-6 showing a broad endothermic process at \( \sim -70 \) °C–5 °C.

This very broad transition is most likely due to the significant volume change of the long branched alkyl chains during re-organization. Nevertheless, it appears that the Tg of PPEV 5-6 lies somewhere in the negative temperatures (around -70 °C), which explains its rubbery appearance at room temperature.

As a result of the interesting thermal properties of PPEV 5-6 we sought out investigations into whether the polymer displays mechano-fluorescence upon applying strain as an external stimulus due to the flexibility of the *trans*-PPEV. This was accomplished by preparing a spin-cast film of 5-6 on a polyvinyl chloride (PVC) flexible substrate from chloroform solution. By slowing increasing the tension while subsequently monitoring the UV-vis and fluorescence spectroscopies we could observe any change in optical characteristics (Figure 5.6). Interestingly, when tension was applied to a spin-cast film of 5-6 at 25% strain, we initially observed a slight decrease in fluorescence intensity.
Figure 5.6. UV-vis (left) and fluorescence (right) spectroscopy of *trans*-PPEV 5-6 deposited on flexible substrate upon applying tension. Spin-cast film prepared from chloroform solution.

However, upon further tension up to 75% strain, we can see a very large increase in fluorescence intensity (large enough where saturation of the detector can not sufficiently measure the fluorescence maximum). It must be noted that there is little to no change in the UV-vis spectra during strain, which would indicate the change is not caused by an increase or decrease in the concentration of fluorophores being excited. While the PPEV 5-6 demonstrates mechano-fluorescent properties, it still must be investigated as to how the quantum efficiency changes quantitatively upon percent strain.

5.3. Conclusions

In conclusion, we developed a synthetic approach to stereoselective preparation of a novel class of fluorescent conjugated polymers PPEVs. While, both *cis*- and *trans*-PPEVs display similar optical properties, they lie in between the spectral characteristics of PPE and PPV conjugated polymers. However, *trans*-PPEV shows a substantially higher fluorescence quantum yield, which is partially due to the high molecular weight and conformationally extended nature of the conjugated backbone. *trans*-PPEV 5-6 also displays interesting physical characteristics in
thin film such as mechano-fluorescence due to its ability to stretch and the mechanical flexibility it possesses.

5.4. References


CHAPTER 6. EXPERIMENTAL SECTION

6.1. General Considerations

All reactions were performed under an atmosphere of dry nitrogen, except those that required Schlenk techniques, which were performed under an atmosphere of ultrapure argon. Melting points were determined in open capillaries and are uncorrected. Chromatographic separations were carried out on silica gel (Sorbent Technologies, 60 Å, 40-63 µM, pH = 6.0-7.0) while reverse phase separations were carried out on C18-silica gel (Sorbent Technologies, 60 Å, 40-63 µM, Endcapped, Carbon Load: 18-22%) slurry packed into glass columns. Toluene, THF, dichloromethane, ether and hexanes were dried by passing through columns of activated alumina and N,N-dimethylformamide (DMF) was dried though a column of molecular sieves both contained in a PS-400 Solvent Purification System from Innovative Technologies, Inc. The water content in the solvents was confirmed by coulometric titration on a Mettler Toledo DL 32 diaphragm-less coulometric titrator. Organometallic reagents were titrated with salicylaldehyde phenylhydrazone prior to use.\(^1\) High purity Pd(PPh\(_3\))\(_4\) was obtained from Strem, while all other reagents were obtained from Sigma-Aldrich and Alfa Aesar and used as received.\(^1\) \(^1\)H NMR spectra were recorded at 400 MHz or 500 MHz unless otherwise indicated and are reported in parts per million downfield from tetramethylsilane. \(^31\)P NMR spectra were obtained at 162 MHz and are reported in ppm relative to 80% aqueous H\(_3\)PO\(_4\) as external standard. GPC analysis of polymers was performed with Agilent 1100 chromatograph equipped with two PLgel 5 µm MIXED-C and one PLgel 5 µm 1000 Å columns connected in series, using THF as a mobile phase, and calibrated against polystyrene standards. GPC analysis of amphiphilic copolymers was performed with Multi-angle Light Scattering (GPC-MALS). Samples were prepared at a concentration of 1.0 mg/mL in THF (stabilized with 250 ppm BHT) using an injection volume of
100 µL (1mL/minute). The separations were carried out using a Gastorr BG-34 degasser, an Agilent 1100 pump, and an Agilent 1100 autosampler. A guard column (10 µm, 50x7.8 mm and two Phenogel 300x7.8 mm columns, Phenomenex, Torrance, CA) connected in series: (1) 10µm, 10^5Å (10-1000 K); (2) 10µ, MXM (100-10,000 K) were used for separations. For detection, a Wyatt Dawn DSP-F multiangle light scattering detector with a He-Ne laser (623.8nm) and Agilent 1200 differential refractive index detector were used. Data acquisition and data processing were performed using the Astra 6 software (Wyatt). UV-visible spectra were recorded on a Varian Cary 50 spectrophotometer or Agilent Cary 5000 spectrophotometer. Fluorescence studies were carried out using a PTI QuantaMaster4/2006SE spectrofluorometer. Quantum yields of soluble organic polymers and spin-cast films were obtained using a Labsphere 3P-GPS-060-SF 6” diameter integration sphere externally attached to a PTI QuantaMaster4/2006SE spectrofluorometer. Fluorescence quantum yields of colloidally dispersed organic nanoparticles were determined relative to 0.1 M H₂SO₄ solution of quinine sulfate (Φ = 0.55²) as a standard. High-powered ultrasonication of organic nanoparticles was carried out using a Branson Sonifier 450 (400 W nominal power) operating at 70% power. Polymer films were prepared by spin coating using Laurell Technologies WS-400B-6NPP spin processor. Thermogravimetric analysis (TGA) of solid polymer samples was performed using TGA 2950 from TA Instruments (New Castle, DE) at the heating rate of 10 °C min⁻¹ in a nitrogen atmosphere. Differential scanning calorimetry of solid polymer samples was performed using a DSC TA 2920 (TA Instruments, Inc., New Castle, USA). Samples were measured in aluminum pans at a rate of 10 °C min, under N₂ gas flow. An empty pan was used as reference, and Indium (99.98%, mp 156.65°C, Aldrich, Milwaube, USA) utilized as the standard for calibrating the temperature. TEM images were obtained on a JEOL JEM-1400 Electron
Microscope instrument (acceleration voltage 120 kV). The TEM samples were prepared by drop-casting from chloroform suspensions on a carbon-copper grid (Electron Microscopy Sciences). Cryo TEM samples were prepared using a Gatan cryo plunge. A volume of 5 µL of the sample was applied to a 300-mesh holey carbon coated TEM grid. Double sided blotting to the grid in 2 seconds left a thin film of the sample on the grid, which was then quickly plunged into liquid ethane chilled by liquid nitrogen. The frozen sample grid was loaded in single tilt liquid nitrogen cryo transfer holder, then inserted to a JEOL JEM-1400 Electron Microscope instrument. Images were taken with Gatan US1000XP2 camera. High-resolution mass spectra were obtained at the Mass Spectrometry Facility at Louisiana State University using an ESI-TOF or MALDI-TOF method with peak matching protocol to determine the mass and error range of the molecular ion. Electrochemical measurements were carried out on an Autolab PGSTAT 302 potentiostat from Eco Chemie. The experiments were carried out using a three-electrode system with Pt button working electrode (diameter 2 mm), Ag/AgNO₃ non-aqueous reference electrode, and a Pt wire counter electrode. The reference electrode was checked against ferrocene standard every time before and after the experiments were performed, and the measured potentials were corrected based on the Fc/Fc⁺ redox potential value. All experiments were carried out in 0.1 M Bu₄NPF₆ solution in THF or DCM as supporting electrolyte.

6.2. X-ray Photoelectron Spectroscopy

XPS experiments of organic nanoparticles were carried out using PHI VersaProbe II instrument equipped with a monochromatic Al K(alpha) source. Instrument base pressure was ca. 8 × 10⁻¹⁰ Torr. The X-ray power of 50 W at 15 kV was used for all experiments with 200 micron beam size at the X-ray incidence and take off angles of 45°. The instrument work function was calibrated to give a binding energy (BE) of 84.0 eV for Au 4f⁷/₂ line for metallic
gold and the spectrometer dispersion was adjusted to give a BE’s of 284.8 eV, 932.7 eV and of 368.3 eV for the C 1s line of adventitious (aliphatic) carbon presented on the non-sputtered samples, Cu 2p\textsubscript{3/2} and Ag 3d\textsubscript{5/2} photoemission lines, respectively. The PHI dual beam charge neutralization system was used on all samples. The high resolution Br 3d and I 4d spectra were taken with a minimum of 100-200 s scans using a 0.1 eV step and 93.9 eV pass energy. The ultimate VersaProbe II instrumental resolution was determined to be better than 0.125 eV using the Fermi edge of the valence band for metallic silver.

Table 6.1. Fitting parameters for Br 3d and I 4d high-resolution XPS spectra.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Transitions</th>
<th>Position, eV</th>
<th>Position separation, eV</th>
<th>FWHM, eV</th>
<th>Area</th>
<th>% Area</th>
<th>Chi Squared</th>
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<tbody>
<tr>
<td>PDCI(1.0)-PT NPs</td>
<td>Br 3d\textsubscript{5/2}</td>
<td>70.76</td>
<td>0.0</td>
<td>1.67</td>
<td>250</td>
<td>57.14</td>
<td>0.93</td>
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<td></td>
<td>Br 3d\textsubscript{3/2}</td>
<td>71.75</td>
<td>1.00</td>
<td>1.60</td>
<td>187</td>
<td>42.86</td>
<td></td>
</tr>
<tr>
<td>PDCI(1.0)-PPP NPs</td>
<td>I 4d\textsubscript{5/2}</td>
<td>50.65</td>
<td>0.0</td>
<td>1.36</td>
<td>108</td>
<td>57.14</td>
<td>0.98</td>
</tr>
<tr>
<td></td>
<td>I 4d\textsubscript{3/2}</td>
<td>52.43</td>
<td>1.77</td>
<td>1.61</td>
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</tr>
<tr>
<td></td>
<td>Br 3d\textsubscript{5/2}</td>
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<td>0.0</td>
<td>1.86</td>
<td>203</td>
<td>57.14</td>
<td>1.13</td>
</tr>
<tr>
<td></td>
<td>Br 3d\textsubscript{3/2}</td>
<td>71.55</td>
<td>0.74</td>
<td>1.76</td>
<td>152</td>
<td>42.86</td>
<td></td>
</tr>
</tbody>
</table>

All XPS spectra were recorded using PHI software SmartSoft –XPS v2.0 and processed using PHI MultiPack v9.0. The relative sensitivity factors from MultiPack library were used to determine atomic percentage. Peaks were fitted using GL line shapes a combination of Gaussians and Lorentzians with 30-50% of Lorentzian contents. Shirley background was used for curve-fitting. The samples were prepared by drop-casting suspensions of nanoparticles in chloroform on a glass and/or silicon wafer substrate. A given sample was examined at 5-6 different spots on the mounted specimen to assure that consistent, reproducible results were obtained.
6.3. Photostability Determinations

Suspensions of organic nanoparticles in water or chloroform with optical absorbance of around 0.2 a.u. in standard 10 mm fluorescence cuvettes were irradiated at the corresponding excitation wavelength (340 nm for PDCI-PT and 310 nm for PDCI-PPP nanoparticles) with an incident light intensity of 1 mW cm\(^{-2}\) for specified periods of time. The incident light with required wavelength and intensity was obtained using a set up consisting of Newport 66353 300W Xe lamp, equipped with Newport 68945 digital exposure controller, and Newport 77250 high throughput monochromator. The light intensity was measured using a Newport 70260 radiant power meter. The samples were irradiated for periods of 10 min with the total irradiation time of 2 h, and fluorescent spectra was measured after every period using a PTI QuantaMaster4/2006SE spectrofluorometer.

6.4. NMR monitoring of 2-5-initiated polymerization of monomer 2-3.

A Grignard monomer 2-3 solution was prepared before the experiment as described in the procedure for polymer 2-9. A solution of catalyst 2-5 (0.9 mL, 30 mM in THF-d\(_8\), 27 µmol) was placed into an NMR tube sealed with a Young Teflon valve (Norell) under Ar atmosphere. This sample was used to adjust shimming and other NMR spectrometer settings so the reaction monitoring could be started immediately after initiating the polymerization. A solution of Grignard monomer 2-3 (0.4 mL of 0.375 M solution in THF, 0.15 mmol) was injected into a separate NMR tube containing a solution of complex 2-5 (0.5 mL, 54 mM in THF, 27 µmol) via syringe through the valve in order to adjust the concentration of 2-5 to 30 mM. The sample was inverted and the \(^{31}\)P NMR spectra were immediately acquired every 5 min during the 1 h period at room temperature.
6.5. Transient Absorption Spectroscopy

![Schematic diagram of the ultrafast transient absorption setup.](image)

The transient absorption setup used an amplified Titanium:Sapphire laser system that produced 75 fs pulses centered at 800 nm with a 10 kHz repetition rate and an average pulse energy of 0.7 mJ. The optical setup included a beam splitter to separate the pump and probe pulses as well as a retroreflector on a computer-controlled translation stage to control the pump-probe temporal delay. The absorption spectra of the nanoparticle suspensions in water were measured as a function of pump-probe time delay using pump pulses of selected wavelengths and UV-vis white light probe pulses. An optical parametric amplifier provided a selected pump pulse wavelength of 350 nm at a power of 5 µJ. The probe beam was used to generate 400 nm by frequency doubling with a nonlinear beta barium borate crystal. The 400 nm and the residual 800 nm pulses were focused into a water flow cell to generate UV-vis femtosecond white light pulses. The pump and probe pulses were focused to a spatial overlap in a 3 mm quartz flow cell. A computer-controlled beam block allowed for background-subtracted ultrafast time-resolved transient absorption data acquisition. Several time-resolved spectral scans were taken for each
sample for statistical analysis. A schematic diagram of the ultrafast transient absorption setup is shown in Figure 6.1. The time-dependent transient absorption profiles over the wavelength range of 320 nm to 380 nm were analyzed with a global analysis technique\textsuperscript{3,4} using double exponential functions to obtain the corresponding decay spectra with two different lifetimes.

6.6. Synthetic Details

**Bis[1,3-bis(diphenylphosphino)propane]nickel(0) (Ni(dppp))** was prepared following the literature procedure.\textsuperscript{5} To a vigorously stirred mixture of 1.50 g (5.84 mmol) of nickel(II) bis(acetylacetonate) (Ni(acac)) and 4.82 g (11.7 mmol) of 1,3-bis(diphenylphosphino)propane (dppp) in 80 mL of ether and 15 mL of toluene, a solution of \textit{i}-Bu\textsubscript{3}Al (19.8 mL of 1.0 M solution in hexanes, 19.8 mmol) was added slowly over a 1 h period (syringe pump) in Ar atmosphere. The resulting mixture was stirred at room temperature for 24 h, and during this period the solution color changed from bright-green to bright-red. The reaction mixture was left to stay unperturbed for additional 24 h, and the resulting precipitate was filtered under nitrogen, and washed with excess ether to give 3.5 g (68\%) of the product as a bright-orange solid material, mp 281 °C, decomp. (lit.\textsuperscript{5} mp 281-283 °C).

Alternatively, **Ni(dppp)** was prepared by ligand exchange between bis(1,5-cyclooctadiene)nickel(0) (Ni(COD)) and dppp. A mixture of 0.5 g (1.8 mmol) of Ni(COD) and 1.5 g (3.64 mmol) of 1,3-bis(diphenylphosphino)propane (dppp) in 10 mL of ether was stirred in Ar atmosphere in a sealed air-free flask at room temperature for 2 h, upon which an orange precipitate formed. The precipitate was filtered and washed with ether (60 mL) under nitrogen to yield 1.12 g (70\%) of the product as a bright-orange solid material, mp 281 °C, decomp. (lit.\textsuperscript{5} mp 281-283 °C).
**General procedure for the preparation of catalytic initiator 2-5.** In a glovebox, a solution of 74 mg (0.3 mmol) of 5-bromo-2,2’-bithiophene 2-4 and 265 mg (0.3 mmol) of Ni(dppp)₂ in 10 mL of THF was stirred for 48 h at 50 °C. The reaction mixture could be precipitated with petroleum ether, centrifuged, and dried in vacuo to collect 97 mg (45%) of 2-5 as a pale-orange solid. ³¹P NMR (162 MHz, THF-d₈) δ 18.6 (d, J = 66 Hz), −3.3 (d, J = 66 Hz). ¹H NMR (400 MHz, THF-d₈) δ 8.03 – 7.14 (m, 20H), 6.93 (dd, J₁ = 5.1, J₂ = 1.1 Hz, 1H), 6.76 (dd, J₁ = 5.1, J₂ = 3.5 Hz, 1H), 6.62 (dd, J₁ = 3.6, J₂ = 1.1 Hz, 1H), 6.46 (d, J = 3.5 Hz, 1H), 6.01 (d, J = 3.5 Hz, 1H), 2.56 – 2.11 (m, 6H).

**Catalytic initiator 2-7** was prepared following the procedure described above for the catalytic initiator 2-5. Reaction of 15 mg (0.09 mmol) of bromobenzene and 80 mg (0.09 mmol) of Ni(dppp)₂ in 5 mL of THF at 40 °C for 48 h produced 30.4 mg (54%) of 2-7 as a pale-yellow solid. ³¹P NMR (162 MHz, THF-d₈) δ 22.0 (d, J = 46 Hz), −3.6 (d, J = 46 Hz). ¹H NMR (400 MHz, THF-d₈) δ 8.05 – 7.11 (m, 20H), 6.92 – 6.82 (m, 2H), 6.35 – 6.25 (m, 2H), 6.24 – 6.15 (m, 1H), 2.57 – 2.09 (m, 6H).

**Representative procedure for externally initiated Kumada polycondensation – preparation of polymer 2-9 (entry 4 in Table 2.1).** A solution of i-PrMgCl (0.42 mL of 2.0 M solution in THF, 0.84 mmol) was added dropwise to a stirred solution of 0.25 g (0.76 mmol) of 2,5-dibromo-3-hexylthiophene in 10 mL of THF at 0 °C, and the resulting solution was stirred for 1 h at this temperature to yield a solution of Grignard reagent 2-3. An aliquot of solution of catalytic initiator 2-5 (0.76 mL of 10 mM solution in THF, 7.6 mmol, 1.0 mol%) was added to the Grignard reagent solution at room temperature. The reaction mixture was stirred at 35 °C for 1 h, then quenched with 5M HCl. Precipitation into 120 mL of methanol followed by separation by centrifugation and drying in vacuo resulted in 95 mg (75%) of 2-9 as a dark-purple solid with
metallic luster, $M_n$ 24 kDa, PDI 1.54 (GPC, vs. polystyrene). $^1$H NMR (500 MHz, CDCl$_3$) δ 6.98 (s, 1H), 2.81 (t, $J = 7.9$ Hz, 2H), 1.82 – 1.58 (m, 2H), 1.50 – 1.21 (m, 6H), 0.99 – 0.81 (m, 3H).

**Block copolymer 2-10.** A solution of $i$-PrMgCl (0.48 mL of 1.41 M solution in THF, 0.67 mmol) was added dropwise to a stirred solution of 0.2 g (0.62 mmol) of 2,5-dibromo-3-hexylthiophene in 10 mL of THF at 0 °C, and the resulting solution was stirred for 1 h at this temperature to yield solution of the Grignard reagent 2-3. An aliquot of initiator solution 2-5 (0.62 mL of 10 mM solution in THF, 6.2 µmol) was added to the Grignard reagent solution and the reaction mixture was stirred at 35 °C for 1 h. A solution of the Grignard reagent 2-8 (prepared separately at 0 °C from 0.25 g (0.62 mmol) of 2-[(2,5-dibromothiophen-3-yl)ethoxy]-**tert**-butyldimethylsilane$^6$ in 10 mL of THF and 0.48 mL (0.67 mmol) of 1.41 M solution of $i$-PrMgCl in THF) was added, and the resulting solution was stirred at 35 °C for additional 1.5 h. Precipitation into 150 mL of methanol resulted in 0.174 g (69%) of 2-10 as a dark-purple solid material with metallic luster, $M_n$ 41 kDa, PDI 1.41 (GPC, vs polystyrene). $^1$H NMR (400 MHz, CDCl$_3$) δ 7.08 (s, 0.71H), 6.98 (s, 1H), 3.91 (t, $J = 6.8$ Hz, 1.43H), 3.04 (t, $J = 6.8$ Hz, 1.43H), 2.80 (t, $J = 7.8$ Hz, 2H), 1.75 – 1.58 (m, 2H), 1.60 – 1.16 (m, 6H), 1.00 – 0.78 (m, 9.43H), 0.12 – –0.04 (m, 4.29H). Based on the $^1$H NMR data, the ratio of P3HT to poly[3-(TBDMSO-ethyl)thiophene] blocks was ~1.4:1.

**Block copolymer 2-11.** A solution of $i$-PrMgCl (0.41 mL of 1.7 M solution in THF, 0.67 mmol) was added dropwise to a stirred solution of 0.25 g (0.62 mmol) of 2-[(2,5-dibromothiophen-3-yl)ethoxy]-**tert**-butyldimethylsilane$^3$ in 10 mL of THF at 0 °C, and the resulting solution was stirred for 1 h at this temperature to yield solution of the Grignard reagent 2-8. An aliquot of initiator solution 2-5 (0.62 mL of 10 mM solution in THF, 6.2 µmol) was added to the Grignard reagent solution and the reaction mixture was stirred at 35 °C for 1 h. A
solution of the Grignard reagent 2-3 (prepared separately at 0 °C from 0.2 g (0.62 mmol) of 2,5-
dibromo-3-hexylthiophene in 10 mL of THF and 0.41 mL (0.67 mmol) of 1.7 M solution of i-
PrMgCl in THF) was added, and the resulting solution was stirred at 35 °C for additional 1.5 h.
Precipitation into 150 mL of methanol resulted in 0.181 g (72%) of 2-11 as a dark-purple solid
material with metallic luster, $M_n$ 41 kDa, PDI 1.46 (GPC, vs polystyrene). $^1$H NMR (400 MHz,
CDCl$_3$) $\delta$ 7.08 (s, 0.83H), 6.98 (s, 1H), 3.91 (t, $J = 6.8$ Hz, 1.67H), 3.04 (t, $J = 6.8$ Hz, 1.67H),
2.80 (t, $J = 7.6$ Hz, 2H), 1.80 – 1.55 (m, 2H), 1.50 – 1.18 (m, 6H), 1.00 – 0.80 (m, 10.5H), 0.14 –
–0.05 (m, 5H). Based on $^1$H NMR, the ratio of P3HT to poly[3-(TBDMSO-ethyl)thiophene]
blocks was ~1.2:1.

**Polymer 2-12 (entry 9 in Table 2.1).** A solution of i-PrMgCl (0.51 mL of 2.0 M solution in
THF, 1.0 mmol) was added dropwise to a stirred solution of 0.3 g (0.9 mmol) of 2,5-dibromo-3-
hexylthiophene in 10 mL of THF at 0 °C, and the resulting solution was stirred for 1 h at this
temperature to yield a solution of Grignard reagent 2-3. An aliquot of solution of catalytic
initiator 2-7 (0.91 mL of 10 mM solution in THF, 9.1 µmol, 1.0 mol%) was added to the
Grignard reagent solution at room temperature. The reaction mixture was stirred at 35 °C for 1
h, then quenched with 5M HCl. Precipitation into 120 mL of methanol followed by separation
by centrifugation and drying in vacuo resulted in 101 mg (66%) of 2-12 as a dark-purple solid
with metallic luster, $M_n$ 27 kDa, PDI 1.25 (GPC, vs. polystyrene). $^1$H NMR (500 MHz, CDCl$_3$)
$\delta$ 6.98 (s, 1H), 2.81 (t, $J = 7.9$ Hz, 2H), 1.86 – 1.55 (m, 2H), 1.54 – 1.17 (m, 6H), 1.06 – 0.77 (m,
3H).

**Polymer 2-13 (entry 10 in Table 2.1).** A solution of i-PrMgCl (0.33 mL of 1.85 M solution
in THF, 0.61 mmol) was added dropwise to a stirred solution of 0.2 g (0.61 mmol) of 2,5-
dibromo-3-hexylthiophene in 8 mL of THF at 0 °C, and the resulting solution was stirred for 1 h
at this temperature to yield a solution of Grignard reagent 2-3. An aliquot of a solution of catalytic initiator 2-5 (0.61 mL of 10 mM solution in THF, 6.1 µmol, 1.0 mol%) was added to the Grignard reagent solution at room temperature. The reaction mixture was stirred at 35 °C for 1 h. Precipitation into 120 mL of methanol followed by separation by centrifugation and drying \textit{in vacuo} resulted in 56 mg (55%) of 2-13 as a dark-purple solid, $M_n$ 16.9 kDa, PDI 2.00 (GPC, vs. polystyrene). $^1$H NMR (500 MHz, CDCl$_3$) δ 6.98 (s, 1H), 2.81 (t, $J = 7.9$ Hz, 2H), 1.82 – 1.58 (m, 2H), 1.50 – 1.21 (m, 6H), 0.99 – 0.81 (m, 3H).

**Polymer 2-13 (quenched with 5 M HCl).** This polymer was synthesized exactly following the procedure for 2-13 above, yet after the polymerization reaction mixture was allowed to stir for 1 h, it was quenched with 5 M HCl, then subsequently precipitated into 120 mL of methanol, separated by centrifugation, and dried \textit{in vacuo} to afford 40 mg (40%) of 2-13 as a dark-purple solid, $M_n$ 12.6 kDa, PDI 2.18 (GPC, vs. polystyrene). $^1$H NMR (500 MHz, CDCl$_3$) δ 6.98 (s, 1H), 2.81 (t, $J = 7.9$ Hz, 2H), 1.82 – 1.58 (m, 2H), 1.50 – 1.21 (m, 6H), 0.99 – 0.81 (m, 3H).

**Polymer 2-14 (entry 11 in Table 2.1).** A solution of $i$-PrMgCl (0.33 mL of 1.85 M solution in THF, 0.61 mmol) was added dropwise to a stirred solution of 0.2 g (0.61 mmol) of 2,5-dibromo-3-hexylthiophene in 8 mL of THF at 0 °C, and the resulting solution was stirred for 1 h at this temperature to yield a solution of Grignard reagent 2-3. An aliquot of solution of catalytic initiator 2-7 (0.61 mL of 10 mM solution in THF, 6.1 µmol, 1.0 mol%) was added to the Grignard reagent solution at room temperature. The reaction mixture was stirred at 35 °C for 1 h. Precipitation into 120 mL of methanol followed by separation by centrifugation and drying \textit{in vacuo} resulted in 40 mg (40%) of 2-14 as a dark-purple solid, $M_n$ 14.0 kDa, PDI 1.75 (GPC, vs. polystyrene). $^1$H NMR (500 MHz, CDCl$_3$) δ 6.98 (s, 1H), 2.81 (t, $J = 7.9$ Hz, 2H), 1.82 – 1.58 (m, 2H), 1.50 – 1.21 (m, 6H), 0.99 – 0.81 (m, 3H).
Polymer 2-14 (quenched with 5 M HCl). This polymer was synthesized following the procedure for the polymer 2-14 above, yet after the polymerization reaction mixture was allowed to stir for 1 h, it was quenched with 5 M HCl, then precipitated into 120 mL of methanol, separated by centrifugation, and dried in vacuo to afford 32 mg (32%) of 2-14 as a dark-purple solid, $M_n$ 11.9 kDa, PDI 1.90 (GPC, vs. polystyrene). $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 6.98 (s, 1H), 2.81 (t, $J$ = 7.9 Hz, 2H), 1.82 – 1.58 (m, 2H), 1.50 – 1.21 (m, 6H), 0.99 – 0.81 (m, 3H).

Preparation of P3HT using large excess of i-PrMgCl. A solution of i-PrMgCl (0.99 mL of 1.85 M solution in THF, 1.8 mmol) was added dropwise to a stirred solution of 0.3 g (0.92 mmol) of 2,5-dibromo-3-hexylthiophene in 10 mL of THF at 0 °C, and the resulting solution was stirred for 1 h at this temperature to yield a solution of Grignard reagent 2-3. An aliquot of a solution of catalytic initiator 2-5 (0.91 mL of 10 mM solution in THF, 9.1 µmol, 1.0 mol%) was added to the Grignard reagent solution at room temperature. The reaction mixture was stirred at 35 °C for 1 h. Precipitation into 120 mL of methanol followed by separation by centrifugation and drying in vacuo resulted in 94 mg (62%) of the polymer as a red/orange solid, $M_n$ 4.2 kDa, PDI 1.59 (GPC, vs. polystyrene). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 6.98 (s, 1H), 2.97 – 2.66 (m, 2H), 1.82 – 1.58 (m, 2H), 1.50 – 1.21 (m, 6H), 0.99 – 0.81 (m, 3H). A similar polymer was also prepared by quenching the polymerization reaction with 5 M HCl, yield 46 mg (30%), $M_n$ 4.1 kDa, PDI 1.58 (GPC, vs. polystyrene).

$N,N'$-Di(2,6-diisopropylphenyl)-1,7-dibromoperylene-3,4:9,10-tetracarboxylic acid bisimide (4-2). Regiochemically pure dibromide 4-1 was prepared following the procedure developed by Würthner et al.\(^7\)

$N,N'$-Di(2,6-diisopropylphenyl)-1,7-di(2,2'-bithien-5-yl)perylene-3,4:9,10-tetracarboxylic acid bisimide (4-3). A solution of 0.84 g (0.96 mmol) of 4-2, 1.14 g (2.5 mmol)
of 2-tributylstannylbithiophene, and 0.13 g (0.19 mmol) of Pd(PPh$_3$)$_2$Cl$_2$ in 14 mL of anhydrous DMF in an air-free flask was heated to 110 °C for 2 days. The reaction mixture was then poured in water and extracted with Et$_2$O, and the organic layer was dried over Na$_2$SO$_4$. Concentration in vacuo gave a crude black solid which was purified by column chromatography on silica gel upon elution with a 2:1 dichloromethane/hexanes mixture to afford 0.75 g (75%) of S2 as a crystalline black solid, $R_f$ 0.41, mp. >300 °C. $^1$H NMR (400 MHz, CD$_2$Cl$_2$) δ 8.76 (d, $J$ = 8.0 Hz, 2H), 8.48 (t, $J$ = 9.7 Hz, 2H), 8.36 (d, $J$ = 8.0 Hz, 2H), 7.65 – 6.94 (m, 16H), 2.88 – 2.64 (m, 4H), 1.40 – 0.96 (m, 24H). HRMS (ESI-TOF) m/z 1038.2660 [M–H$^+$]$^-$ (calcd. for C$_{64}$H$_{50}$N$_2$O$_4$S$_4$ 1038.2659).

$N,N'$-Di(2,6-diisopropylphenyl)-1,7-di(5'-bromo-2,2'-bithien-5-yl)perylene-3,4:9,10-tetracarboxylic acid bisimide (3-1 and 4-4). $N$-Bromosuccinimide (0.31 g, 1.7 mmol) was added in small portions over ~5 min to a stirred solution of 0.75 g (0.7 mmol) of 4-3 in 80 mL of THF, and the resulting mixture was stirred at room temperature for 24 h. The reaction mixture was poured in water and extracted with Et$_2$O, and the organic layer was dried over Na$_2$SO$_4$ and concentrated in vacuo. The crude solid was purified by column chromatography on silica gel upon elution with a 3:1 dichloromethane/hexanes mixture to yield 0.66 g (77%) of 1 as a black crystalline solid, $R_f$ 0.6, mp. 293-295 °C. $^1$H NMR (400 MHz, CD$_2$Cl$_2$) δ 8.82 – 8.66 (m, 2H), 8.55 – 8.40 (m, 2H), 8.41 – 8.31 (m, 2H), 7.61 – 7.45 (m, 2H), 7.45 – 7.28 (m, 6H), 7.28 – 7.15 (m, 3H), 7.10 – 6.94 (m, 3H), 2.86 – 2.64 (m, 4H), 1.36 – 0.96 (m, 24H). HRMS (ESI-TOF) m/z 1194.0862 [M–H$^+$]$^-$ (calcd. for C$_{64}$H$_{48}$Br$_2$N$_2$O$_4$S$_4$ 1194.0869).

Catalytic initiator 3-2 and 4-5 was prepared by stirring a mixture of 0.04 g (0.03 mmol) of dibromide 3-1/4-4 with 0.09 g (0.1 mmol) of Ni(dppp)$_2$ in 3 mL of dry THF under inert atmosphere for 3 h at room temperature and used as obtained, without further purification.
NMR (162 MHz, THF) δ 18 (br. m, 1P), –5 (br. m, 1P). The broad signals in $^{31}$P NMR spectrum could be explained by poor solubility and/or aggregation of the compound 3-2/4-5.

$N,N'$-Di(2,6-diisopropylphenyl)-1,7-di(2,2':5',2''-terthiophen-5-yl)perylene-3,4:9,10-tetracarboxylic acid bisimide (3-3). A mixture of 0.04 g (0.03 mmol) of 3-1/4-5 and 0.09 g (0.1 mmol) of Ni(dppp)$_2$ in 5 mL of anhydrous THF was stirred in an air-free flask at room temperature for 2 h. A solution of thiophen-2-ylmagnesium chloride (1 mL of 0.1 M solution in THF, 0.1 mmol) was added dropwise, and the reaction mixture was stirred for 1 h at room temperature. The reaction was quenched with 5 M HCl and poured into dichloromethane. The organic fraction was washed thoroughly with water, and dried over Na$_2$SO$_4$. Concentration in vacuo gave the crude product which was dissolved in minimal amount of CH$_2$Cl$_2$ and passed through a plug of silica gel eluted with dichloromethane. This yielded 23.2 mg (58%) of 3-3 as a black crystalline solid, mp. 168-172 °C. $^1$H NMR (400 MHz, CD$_2$Cl$_2$) δ 8.85 – 8.69 (m, 2H), 8.57 – 8.29 (m, 4H), 7.66 – 6.91 (m, 20H), 2.91 – 2.64 (m, 4H), 1.32 – 1.02 (m, 24H).

Polymer 3-7 and 4-9. A solution of i-PrMgCl (0.42 mL of 2 M solution in THF, 0.84 mmol) was added dropwise to a stirred solution of 0.25 g (0.76 mmol) of 2,5-dibromo-3-hexylthiophene in 12 mL of THF and stirred at 0 °C for 1 h. An aliquot of catalytic initiator 3-2/4-5 (prepared as described above, 3 mL of solution in THF, 7.6 µmol, 1 mol %) was added to the Grignard reagent solution and the reaction mixture was stirred for 1 h at 30 °C. After the polymerization was complete, the reaction mixture was quenched with 250 µL of 5 M HCl and precipitated into 150 mL of methanol. The resulting precipitate was separated by centrifugation and washed with methanol to yield 0.11 g (86%) of 3-7 as a purple solid with metallic luster, $M_n$ 12.5 kDa, PDI 1.06 (GPC, vs. polystyrene standards). $^1$H NMR (400 MHz, CDCl$_3$) δ 8.82 – 8.68 (m, 0.03H),
8.53 – 8.32 (m, 0.06H), 7.60 – 6.90 (m, 0.24H), 6.98 (s, 1H), 2.95 – 2.66 (m, 2H), 1.79 – 1.53 (m, 2H), 1.50 – 1.22 (m, 6.36H), 1.04 – 0.76 (m, 3H).

**PDCI(3.0)-PT nanoparticles.** A solution of i-PrMgCl (0.74 mL of 1.75 M solution in THF, 1.3 mmol) was added dropwise to a stirred solution of 0.30 g (1.24 mmol) of 2,5-dibromothiophene in 24 mL of THF at 0 °C, and the resulting solution was stirred for 1 h at this temperature to yield a solution of Grignard reagent 3-5. A solution of catalytic initiator 3-2 (3 mL, 37.2 mmol, 3.0 mol %) was added to the Grignard reagent solution at room temperature upon ultrasonication. The reaction mixture was stirred for ~1.5 min when a precipitate began to appear. After stirring for 10 min with gradual heating to 30 °C, the reaction mixture was quenched with 500 μL of 5 M HCl. The reaction mixture was added into methanol followed by separation by centrifugation, the polymer solid was washed extensively with methanol until supernatant was colorless, and dried in vacuo to yield 72 mg (70%) of PDCI(3.0)-PT nanoparticles as a maroon solid. A small portion (~2-3 mg) of the solid was suspended in 4 mL of CHCl₃ upon ultrasonication for 30 min, and the resulting suspension was filtered through a 0.2 mm syringe filter to produce a CHCl₃ suspension of PDCI(3.0)-PT NPs. To prepare an aqueous suspension, a suspension of PDCI(3.0)-PT NPs was prepared in 2 mL of THF as described above for the CHCl₃ suspension, and injected in 4 mL of DI water upon ultrasonating. The resulting mixture was concentrated at room temperature in vacuo on a rotary evaporator to remove THF, and the produced aqueous suspension was filtered through a 0.2 mm syringe filter to yield the aqueous suspension of PDCI(3.0)-PT nanoparticles.

**PDCI(1.0)-PT nanoparticles** were prepared following the same procedure as described above for PDCI(3.0)-PT nanoparticles using 3 mL (12.4 μmol, 1 mol %) of a THF solution of initiator 3-2. Yield 97 mg (95%).
**PDCI(0.1)-PT nanoparticles** were prepared following the same procedure as described above for PDCI(3.0)-PT nanoparticles using 3 mL (1.2 µmol, 0.1 mol %) of a THF solution of initiator 3-2. Yield 32 mg (32%).

**PDCI(3.0)-PPP nanoparticles.** A solution of \(i\)-PrMgCl (0.63 mL of 1.75 M solution in THF, 1.11 mmol) was added dropwise to a stirred solution of 0.30 g (1.06 mmol) of 1-bromo-4-iodobenzene in 24 mL of THF at 0 °C, and the resulting solution was stirred for 1 h at this temperature to yield solution of the Grignard reagent 3-6. An aliquot of the catalytic initiator 3-2 solution (3 mL of solution in THF, 31.8 mmol, 3.0 mol %) was added to the Grignard reagent solution upon ultrasonication, and the reaction mixture was stirred for 10 min while gradually heating to 30 ºC before quenching with 500 µL of 5 M HCl. The resulting mixture was poured to methanol and the precipitate was collected by centrifugation, washed extensively with methanol, and dried *in vacuo* to yield 61 mg (76%) of PDCI(3.0)-PPP nanoparticles as a black-green solid material. PDCI(3.0)-PPP NP suspensions in CHCl₃ and water were prepared as described above for PDCI(3.0)-PT nanoparticles.

**PDCI(1.0)-PPP nanoparticles** were prepared following the same procedure as described above for PDCI(3.0)-PPP nanoparticles using 3 mL (10.6 µmol, 1 mol %) of a THF solution of initiator 3-2. Yield 48 mg (60%).

**PDCI(0.1)-PPP nanoparticles** were prepared following the same procedure as described above for PDCI(3.0)-PPP nanoparticles using 3 mL (1.1 µmol, 0.1 mol %) of a THF solution of initiator 3-2. Yield 34 mg (43%).

**Preparation of P3HT nanoparticles by reprecipitation method** was done using a procedure in ref. 9. A sample of 10 mg of regioregular P3HT \((M_r 12 \text{ kDa}, \text{PDI } 1.2, \text{regioregularity } >99\%\), prepared as described in ref. 10) and (for PDCI/P3HT NPs) the amount of
PDCI “core” compound 3-1 corresponding to 0.1, 1.0, or 3.0 mol % of PDCI were dissolved in 10 g (11.25 mL) of THF and stirred at room temperature overnight. The resulting solution was filtered through a 0.4 mm syringe filter and an aliquot of 2 mL was further diluted to 20 ppm polymer concentration (100 mL total volume, total polymer concentration ~0.6 mM). An aliquot of 2 mL of the dilute polymer solution was quickly added to 8 mL of water during ultrasonication. The THF was removed by rotary evaporation and the resulting NP solution was filtered through a 0.2 µm syringe filter.

**Preparation of 3-7 nanoparticles by miniemulsion method** was carried out as described in ref. 11. A sample of 15 mg of polymer 3-7 was dissolved in 0.2 mL of CHCl$_3$ and added to 10 mL of 0.055% aqueous solution of sodium dodecyl sulfate. The resulting biphasic solution was stirred for 1 h and then was ultrasonicated for 5 min. The miniemulsion solution was then stirred at 62 °C for 3 h to remove CHCl$_3$, and finally filtered through a 0.2 mm syringe filter.

**PDCI AB block copolymer 4-10.** A solution of $i$-PrMgCl (0.42 mL of 2.0 M solution in THF, 0.84 mmol) was added dropwise to a stirred solution of 0.25 g (0.76 mmol) of 2,5-dibromo-3-hexylthiophene in 10 mL of THF at 0 °C, and the resulting solution was stirred for 1 h at this temperature to yield solution of the Grignard reagent 4-7. An aliquot of initiator solution 4-5 (7.6 µmol in 3 mL THF, 1 mol%) was added to the Grignard reagent solution and the reaction mixture was stirred at 35 °C for 1 h. A solution of the Grignard reagent 4-8 (prepared separately at 0 °C from 0.3 g (0.76 mmol) of 2-[(2,5-dibromothiophen-3-yl)ethoxy]-tert-butyldimethylsilane in 10 mL of THF and 0.42 mL (0.84 mmol) of 2.0 M solution of $i$-PrMgCl in THF) was added, and the resulting solution was stirred at 35 °C for additional 1.5 h. Precipitation into 150 mL of methanol resulted in a crude dark purple polymer which was placed into a Soxhlet extractor, and extracted successively with methanol, hexanes, and chloroform.
The chloroform fraction yielded 0.154 g (50%) of **4-10** as a dark-purple solid material with metallic luster, \( M_n 13.5 \text{ kDa}, \) PDI 1.32 (GPC, vs polystyrene). \(^1\text{H NMR (400 MHz, CDCl}_3) \delta 7.08 (s, 1H), 6.98 (s, 1H), 3.97 – 3.83 (m, 2H), 3.11 – 2.95 (m, 2H), 2.89 – 2.69 (m, 2H), 1.77 – 1.12 (m, 11H), 1.00 – 0.77 (m, 9H), 0.09 – 0.04 (m, 6H). Based on the \(^1\text{H NMR data, the ratio of P3HT to poly[3-(TBDMSO-ethyl)thiophene] blocks was ~1.7:1.**

**PDCI statistical copolymer 4-11.** A solution of \( i\)-PrMgCl (0.96 mL of 1.75 M solution in THF, 1.68 mmol) was added dropwise to a mixed solution of 0.25 g (0.76 mmol) of 2,5-dibromo-3-hexylthiophene and 0.3 g (0.76 mmol) of 2-((2,5-dibromothiophen-3-yl)ethoxy)-tert-butyl(dimethyl)silane in 20 mL of THF at 0 °C. The resulting solution was stirred for 1 h at this temperature to yield a combined solution of Grignard reagents 4-7 and 4-8. An aliquot of initiator solution 4-5 (7.6 µmol in 3 mL THF, 1 mol%) was added to the Grignard reagent solution and the reaction mixture was stirred at 35 °C for 2.5 h. Precipitation into 150 mL of methanol resulted in a crude purple polymer which was placed into a Soxhlet extractor, and extracted successively with methanol, hexanes, and chloroform. The chloroform fraction yielded 0.137 g (38%) of **4-11** as a purple solid material, \( M_n 29.3 \text{ kDa}, \) PDI 1.25 (GPC, vs polystyrene). \(^1\text{H NMR (400 MHz, CDCl}_3) \delta 7.13 – 6.91 (m, 2H), 3.97 – 3.83 (m, 2H), 3.12 – 2.95 (m, 2H), 2.89 – 2.69 (m, 2H), 1.78 – 1.18 (m, 11H), 1.00 – 0.78 (m, 9H), 0.12 – 0.06 (m, 6H). Based on the \(^1\text{H NMR data, the ratio of P3HT to poly[3-(TBDMSO-ethyl)thiophene] blocks was ~1.2:1.**

**PDCI deuterated block copolymer 4-12.** A solution of \( i\)-PrMgCl (0.4 mL of 2.0 M solution in THF, 0.80 mmol) was added dropwise to a stirred solution of 0.26 g (0.76 mmol) of 2,5-dibromo-3-hexylthiophene-\(d_{13}\) in 10 mL of THF at 0 °C, and the resulting solution was stirred for 1 h at this temperature to yield solution of the Grignard reagent **4-7-d\(13\).** An aliquot of initiator solution 4-5 (7.6 µmol in 3 mL THF, 1 mol%) was added to the Grignard reagent...
solution and the reaction mixture was stirred at 35 °C for 1 h. A solution of the Grignard reagent 4-8 (prepared separately at 0 °C from 0.3 g (0.76 mmol) of 2-[(2,5-dibromothiophen-3-yl)ethoxy]-tert-butyl(dimethyl)silane in 10 mL of THF and 0.4 mL (0.80 mmol) of 2.0 M solution of i-PrMgCl in THF) was added, and the resulting solution was stirred at 35 °C for additional 1.5 h. A small aliquot was added to 10 mL of methanol for characterization. The remainder of 4-12 in solution was used in the next step without further purification, $M_n$ 13.5 kDa, PDI 1.54 (GPC, vs polystyrene). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.08 (s, 1H), 6.97 (s, 1H), 3.98 – 3.79 (m, 2H), 3.15 – 2.92 (m, 2H), 1.08 – 0.72 (m, 9H), 0.14 – -0.12 (m, 6H).

**PDC1 BA block copolymer 4-13.** A solution of i-PrMgCl (0.42 mL of 2.0 M solution in THF, 0.84 mmol) was added dropwise to a stirred solution of 0.3 g (0.76 mmol) of 2-[(2,5-dibromothiophen-3-yl)ethoxy]-tert-butyl(dimethyl)silane in 10 mL of THF at 0 °C, and the resulting solution was stirred for 1 h at this temperature to yield solution of the Grignard reagent 4-8. An aliquot of initiator solution 4-5 (7.6 µmol in 3 mL THF, 1 mol%) was added to the Grignard reagent solution and the reaction mixture was stirred at 35 °C for 1 h. A solution of the Grignard reagent 4-7 (prepared separately at 0 °C from 0.25 g (0.76 mmol) of 2,5-dibromo-3-hexylthiophene in 10 mL of THF and 0.42 mL (0.84 mmol) of 2.0 M solution of i-PrMgCl in THF) was added, and the resulting solution was stirred at 35 °C for additional 1.5 h. Precipitation into 150 mL of methanol resulted in a crude dark-purple polymer which was placed into a Soxhlet extractor, and extracted successively with methanol, hexanes, and chloroform. The chloroform fraction yielded 0.174 g (56%) of 4-13 as a dark-purple solid material with a metallic luster, $M_n$ 15.1 kDa, PDI 1.17 (GPC, vs polystyrene). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.08 (s, 1H), 6.98 (s, 1H), 3.97 – 3.84 (m, 2H), 3.10 – 2.97 (m, 2H), 2.86 – 2.71 (m, 2H), 1.77 –
1.62 (m, 2H), 1.51 – 1.20 (m, 9H), 1.02 – 0.77 (m, 9H), 0.11 – 0.05 (m, 6H). Based on the $^1$H NMR data, the ratio of P3HT to poly[3-(TBDMSO-ethyl)thiophene] blocks was ~1.3:1.

**Bithiophene AB block copolymer 4-14.** A solution of i-PrMgCl (0.6 mL of 1.41 M solution in THF, 0.84 mmol) was added dropwise to a stirred solution of 0.25 g (0.76 mmol) of 2,5-dibromo-3-hexylthiophene in 10 mL of THF at 0 °C, and the resulting solution was stirred for 1 h at this temperature to yield solution of the Grignard reagent 4-7. An aliquot of initiator solution 4-6 (1.53 mL of 10 mM solution in THF, 15.3 µmol) was added to the Grignard reagent solution and the reaction mixture was stirred at 35 °C for 1 h. A solution of the Grignard reagent 4-8 (prepared separately at 0 °C from 0.3 g (0.76 mmol) of 2-[(2,5-dibromothiophen-3-yl)ethoxy]-tert-butyldimethylsilane in 10 mL of THF and 0.6 mL (0.84 mmol) of 1.41 M solution of i-PrMgCl in THF) was added, and the resulting solution was stirred at 35 °C for additional 1.5 h. Precipitation into 150 mL of methanol resulted in a crude dark-purple polymer which was placed into a Soxhlet extractor, and extracted successively with methanol, hexanes, and chloroform. The chloroform fraction yielded 0.175 g (57%) of 4-14 as a dark-purple solid material with a metallic luster, $M_n$ 23.2 kDa, PDI 1.58 (GPC, vs polystyrene). $^1$H NMR (400 MHz, CDCl$_3$) δ 7.08 (s, 1H), 6.98 (s, 1H), 3.98 – 3.80 (m, 2H), 3.11 – 2.93 (m, 2H), 2.91 – 2.68 (m, 2H), 1.79 – 1.60 (m, 2H), 1.52 – 1.17 (m, 9H), 1.02 – 0.75 (m, 9H), 0.12 – -0.09 (m, 6H). Based on the $^1$H NMR data, the ratio of P3HT to poly[3-(TBDMSO-ethyl)thiophene] blocks was ~1.5:1.

**PDCI AB block macroinitiator 4-15.** A solution of tetrabutylammonium fluoride (18 mL of 0.1 M solution in THF, 1.8 mmol) was added dropwise over the period of 2 h via syringe pump to a mixture of 0.124 g (0.51 mmol based on repeating unit) of polymer 4-10, 2-isobutyrl bromide 0.64 mL (5.1 mmol), and 0.25 mL of triethylamine (1.8 mmol) in 35 mL of THF at
room temperature. The resulting mixture was allowed to stir at room temperature overnight. Precipitation into 100 mL of methanol resulted in a crude dark-purple polymer which was placed into a Soxhlet extractor, and extracted successively with methanol, hexanes, and chloroform. The chloroform fraction yielded 0.135 g (95%) of 4-15 as a dark-purple solid material with a metallic luster, $M_n$ 15.1 kDa, PDI 1.7 (GPC, vs polystyrene). $^1$H NMR (400 MHz, CDCl$_3$) δ 7.17 (s, 1H), 6.98 (s, 1H), 4.54 – 4.32 (m, 2H), 3.31 – 3.08 (m, 2H), 2.92 – 2.65 (m, 2H), 2.01 – 1.82 (m, 6H), 1.76 – 1.15 (m, 8H), 1.01 – 0.74 (m, 3H).

**Macronitiators 4-16, 4-17, 4-18 and 4-19** were all prepared following a very similar procedure for 4-15 starting from 4-11, 4-12, 4-13 and 4-14, respectively. 4-16: 90% yield, $M_n$ 25.7 kDa, PDI 1.45 (GPC, vs polystyrene). $^1$H NMR (400 MHz, CDCl$_3$) δ 7.18 – 6.88 (m, 2H), 4.62 – 4.31 (m, 2H), 3.37 – 3.07 (m, 2H), 2.91 – 2.65 (m, 2H), 1.93 (s, 6H), 1.80 – 1.59 (m, 2H), 1.52 – 1.20 (m, 6H), 1.06 – 0.75 (m, 3H). 4-17: 83% yield, $M_n$ 11.5 kDa, PDI 1.4 (GPC, vs polystyrene). $^1$H NMR (400 MHz, CDCl$_3$) δ 7.17 (s, 1H), 6.97 (s, 1H), 4.58 – 4.30 (m, 2H), 3.33 – 3.10 (m, 2H), 1.93 (s, 6H). 4-18: 93% yield, $M_n$ 13.9 kDa, PDI 1.25 (GPC, vs polystyrene). $^1$H NMR (400 MHz, CDCl$_3$) δ 7.17 (s, 1H), 6.98 (s, 1H), 4.54 – 4.38 (m, 2H), 3.31 – 3.14 (m, 2H), 2.90 – 2.69 (m, 2H), 1.98 – 1.82 (m, 6H), 1.77 – 1.09 (m, 8H), 0.98 – 0.81 (m, 3H). 4-19: 89% yield, $M_n$ 23.8 kDa, PDI 1.7 (GPC, vs polystyrene). $^1$H NMR (400 MHz, CDCl$_3$) δ 7.17 (s, 1H), 6.98 (s, 1H), 4.57 – 4.38 (m, 2H), 3.32 – 3.14 (m, 2H), 2.91 – 2.71 (m, 2H), 1.93 (s, 6H), 1.77 – 1.10 (m, 8H), 1.02 – 0.68 (m, 3H).

**Amphiphilic polythiophene block copolymer 4-20.** An air-free Schlenk flask was charged with 26 mg (0.18 mmol) of CuBr, 2.05 g (18 mmol) of N-isopropylacrylamide, and 47 mg (0.18 mmol) of 1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane and evacuated. The flask was backfilled and evacuated ~3x then filled with 30 mL of THF, cooled to 0 °C in an ice bath, and
purged with Ar for ~10 min. After 15 min, a separately prepared and degassed air-free flask filled with solution of 50 mg (0.18 mmol based on repeating unit) of 4-15 in 35 mL of THF was added quickly via syringe. The resulting mixture was allowed to stir at 0 °C for 2.5 h, then was precipitated in 200 mL of hexanes. The precipitate was washed thoroughly with diethyl ether, redissolved in THF, and precipitated again into hexanes. Finally, the polymer was dissolved in THF and filtered through a short plug of silica gel eluting with THF to remove any catalyst. The THF solution was precipitated into hexanes and dried to afford 0.7 g (34%) of 4-20 as a light-purple solid material, $M_n$ 165 kDa, PDI 1.01 (GPC using static light-scattering detector). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 6.93 – 5.75 (m, 1H), 4.16 – 3.79 (m, 1H), 2.45 – 1.30 (m, 3H), 1.29 – 0.86 (m, 6H).

**Amphiphilic polythiophene copolymers 4-21, 4-22, 4-23 and 4-24** were all prepared following a very similar procedure for 4-20 starting from 4-16, 4-17, 4-18 and 4-19, respectively. 

4-21: 35% yield, $M_n$ 227 kDa, PDI 1.06 (GPC using static light-scattering detector). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 6.86 – 5.71 (m, 1H), 4.21 – 3.78 (m, 1H), 2.38 – 1.39 (m, 3H), 1.36 – 0.78 (m, 6H). 

4-22: 37% yield, $M_n$ 133 kDa, PDI 1.02 (GPC using static light-scattering detector). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 6.79 – 5.79 (m, 1H), 4.15 – 3.79 (m, 1H), 2.37 – 1.42 (m, 3H), 1.36 – 0.80 (m, 6H). 

4-23: 39% yield, $M_n$ 163 kDa, PDI 1.03 (GPC using static light-scattering detector). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 6.78 – 5.83 (m, 1H), 4.15 – 3.76 (m, 1H), 2.38 – 1.46 (m, 3H), 1.39 – 0.84 (m, 6H).

4-24: 30% yield, $M_n$ 89 kDa, PDI 1.08 (GPC using static light-scattering detector). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 6.90 – 5.71 (m, 1H), 4.15 – 3.78 (m, 1H), 2.33 – 1.46 (m, 3H), 1.39 – 0.81 (m, 6H).
**1,4-Dibromo-2,5-bis(2-decyl-1-tetradecyloxy)benzene.** A mixture of 3.0 g (11 mmol) of dibromohydroquinone,\(^\text{12}\) 11.7 g (28 mmol) of 2-decyl-1-tetradecylbromide,\(^\text{13}\) 6.2 g (45 mmol) of K\(_2\)CO\(_3\), and 1.8 g (11 mmol) of KI in 100 mL of methyl ethyl ketone was stirred at reflux for 2 days. After allowing to cool to room temperature, the reaction mixture was filtered and washed with CH\(_2\)Cl\(_2\). Purification with column chromatography eluting with hexanes results in 9.43 g (90%) of a colorless oil. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.07 (s, 2H), 3.81 (d, \(J = 5.5\) Hz, 4H), 1.89 – 1.69 (m, 2H), 1.56 – 1.16 (m, 86H), 0.94 – 0.76 (m, 6H).

**1,4-diethynyl-2,5-bis(2-decyl-1-tetradecyloxy)benzene (5-1).** A mixture of 1.2 g (1.27 mmol) of 1,4-Dibromo-2,5-bis(2-decyl-1-tetradecyloxy)benzene, 0.45 mL (3.18 mmol) of TMS-acetylene, 74 mg (64 \(\mu\)mol) of Pd(PPh\(_3\))\(_4\), and 12 mg (64 \(\mu\)mol) of CuI in 15 mL of toluene – iPr\(_2\)NH (7:3) mixture was stirred in a sealed Air-free flask at 70 °C for 16 h. After allowing to cool to room temperature, the crude product was concentrated \(\text{in vacuo}\) and passed through a short plug of silica gel using chloroform as an eluent to afford 1.26 g of a brown solid. The solid was dissolved in 30 mL of THF, and a solution of 1.26 g (1.3 mmol) of KOH in 15 mL of methanol was added dropwise at 0 °C to the THF solution and the resulting mixture was stirred for 1 h. The reaction mixture was poured into water and extracted with ethyl acetate. The organic phase was washed with water, brine then water again and dried over Na\(_2\)SO\(_4\). Concentration \(\text{in vacuo}\) afforded a crude product, which was purified by stirring in 5 mL of methyl ethyl ketone containing a suspension of Merrifield resin (4.38 mmol Cl/g) and 78 mg (0.52 mmol) of NaI.\(^\text{14}\) After stirring overnight, the reaction was filtered and the filtrate was concentrated. Further purification via column chromatography (5% ethyl acetate in hexanes) yielded 0.97 g (91% over 2 steps) of 5-1 as a tan waxy solid. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 6.93 (s, 2H), 3.83 (d, \(J = 5.7\) Hz, 4H), 3.29 (s, 2H), 1.90 – 1.71 (m, 2H), 1.56 – 1.15 (m, 86H), 0.88 (t, \(J = 6.7\) Hz, 6H).
4,6-Bis[(diphenylphosphanyl)methyl]-1,3-dibromobenzene (5-2). Ligand 5-2 was synthesized following modified literature procedures.\textsuperscript{15-17} \textsuperscript{31}P NMR (162 MHz, CDCl\textsubscript{3}) δ –12.4. \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) δ 7.65 (s, 1H), 7.41 – 7.27 (m, 20H), 6.38 – 6.23 (m, 1H), 3.28 (s, 4H).

(Z)-1,4-Diphenyl-1-buten-3-yn (5-3). To a solution of [RuCl\textsubscript{2}(PPh\textsubscript{3})\textsubscript{3}] (28.0 mg, 29.4 µmol) metal precursor in toluene (5 mL), ligand 5-2 (18.0 mg, 29.4 µmol) was added. The resulting green colored solution was refluxed for 1h at 110 °C under N\textsubscript{2} atmosphere. At this stage phenylacetylene (0.1 g, 0.98 mmol) was injected to the above reaction mixture and continued reflux for 48 h at the same temperature. The resultant dark brown colored solution was cool down to room temperature and evaporated in vacuum before subjected to characterization without further purification to afford 0.07 g (70%) of desired product 5-3. \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) δ 7.97 (d, J = 7.2 Hz, 2H), 7.57 – 7.31 (m, 8H), 6.74 (d, J = 11.9 Hz, 1H), 5.96 (d, J = 11.9 Hz, 1H).

General Synthesis of Z-vinylene PPEV (5-4 and 5-5). In an Air-free flask was added 90 µmol of 5-1, 8.7 mg (9 µmol) of RuCl\textsubscript{2}(PPh\textsubscript{3})\textsubscript{3}, 9 µmol of the corresponding ligand (5-2 or dppf), and 5 mL of toluene. The reaction is allowed to stir at reflux for 3 days. The reaction mixture is then added dropwise to ~100 mL of MeOH. The solid material is centrifuged and washed with MeOH then dried to collect a sticky red semi-solid material. Purification was accomplished by reverse-phase column chromatography (20% MeOH in THF) to afford 6 mg (6%) of 5-4 and 5-5 as a sticky red semi-solid. \textsuperscript{1}H NMR (400 MHz, CD\textsubscript{2}Cl\textsubscript{2}) δ 7.86 – 6.46 (m, 4H), 4.10 – 3.40 (m, 4H), 1.93 – 1.72 (m, 2H), 1.70 – 0.65 (m, 92H).

General Synthesis of E-vinylene (PPEV) (5-6). In an Air-free flask was added 0.1 g (0.12 mmol) of 5-1, 10.6 mg (12 µmol) of Pd(IPr)\textsubscript{2},\textsuperscript{18} 5.3 mg (12 µmol) of TDMPP, and 5 mL of
toluene. The reaction is allowed to stir at 60 °C for 2 days. The reaction mixture is then added dropwise to ~100 mL of MeOH. The solid material was centrifuged and washed with MeOH then dried to collect 89.1 mg (89%) of an elastomeric orange solid. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.04 – 6.80 (m, 2H), 6.66 – 6.35 (m, 2H), 3.99 – 3.69 (m, 4H), 1.95 – 1.70 (m, 2H), 1.68 – 0.63 (m, 92H).

6.7. References


(16) Dilworth, J. R.; Zheng, Y.; Griffiths, D.V. Binuclear complexes with ligands based on the 2,6-bis(diphenyl-phosphinomethyl)benzene framework. Syntheses and crystal structures of \([\text{Ir}_2\text{Cl}_2(\mu-\text{CO})\{2,6-(\text{Ph}_2\text{PCH}_2)\text{C}_6\text{H}_3\text{S}\}_2\}2\text{CH}_2\text{Cl}_2, \quad [\text{Ni}_2\{2,6-(\text{Ph}_2\text{PCH}_2)\text{C}_6\text{H}_4\text{S}\}_2\}[\text{PF}_6]_2\cdot\text{Et}_2\text{O}0.5\text{CH}_2\text{Cl}_2\) and \([\text{Rh}_2\text{Cl}_2(\text{CO})_2\{1,3-(\text{Ph}_2\text{PCH}_2)\text{C}_6\text{H}_4\}_2\}].\) J.Chem. Soc., Dalton Trans. 1999, 11, 1877-1882.


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Compound 2-5 (400 MHz, THF-d$_8$)
Compound 2-5 (162 MHz, THF)
Compound 2-7 (400 MHz, THF-d₈)
Compound 2-7 (162 MHz, THF)
Compound 2-9 (500 MHz, CDCl₃; entry 1 in Table 2.1)
Compound 2-9 (500 MHz, CDCl$_3$; entry 2 in Table 2.1)
Compound 2-9 (500 MHz, CDCl₃; entry 3 in Table 2.1)
Compound 2-9 (500 MHz, CDCl₃; entry 4 in Table 2.1)
Compound 2-9 (400 MHz, CDCl₃; entry 5 in Table 2.1)
Compound 2-10 (400 MHz, CDCl₃; entry 6 in Table 2.1)
Compound 2-11 (400 MHz, CDCl₃; entry 7 in Table 2.1)
Compound 2-12 (500 MHz, CDCl₃; entry 8 in Table 2.1)
Compound 2-12 (500 MHz, CDCl₃; entry 9 in Table 2.1)
Compound 2-13 (500 MHz, CDCl₃; entry 10 in Table 2.1)
Compound 2-13 (500 MHz, CDCl₃; Quenched with 5 M HCl)
Compound 2-14 (500 MHz, CDCl₃; entry 11 in Table 2.1)
Compound 2-14 (500 MHz, CDCl₃; Quenched with 5 M HCl)
Compound 2-9 (400 MHz, CDCl₃; 2 eq. excess of i-PrMgCl, Quenched in MeOH)
Compound 2-9 (400 MHz, CDCl₃; 2 eq. excess of i-PrMgCl, Quenched in 5 M HCl)
Compound 4-2 (400 MHz, CDCl₃)
Compound 4-3 (400 MHz, CD$_2$Cl$_2$)
Compound 3-1 and 4-4 (400 MHz, CD$_2$Cl$_2$)
Compound 3-2 and 4-5 (162 MHz, THF)
Compound 3-3 (400 MHz, CD₂Cl₂)
Compound 3-7 and 4-9 (400 MHz, CDCl$_3$)
Compound 4-10 (400 MHz, CDCl$_3$)
Compound 4-11 (400 MHz, CDCl$_3$)
Compound 4-12 (400 MHz, CDCl₃)
Compound 4-13 (400 MHz, CDCl₃)
Compound 4-14 (400 MHz, CDCl₃)
Compound 4.15 (400 MHz, CDCl₃)
Compound 4-16 (400 MHz, CDCl$_3$)
Compound 4-17 (400 MHz, CDCl₃)
Compound 4-18 (400 MHz, CDCl₃)
Compound 4-19 (400 MHz, CDCl₃)
Compound 4-20 (400 MHz, CDCl₃)
Compound 4-21 (400 MHz, CDCl₃)
Compound **4-22** (400 MHz, CDCl$_3$)
Compound 4-23 (400 MHz, CDCl₃)
Compound **4-24** (400 MHz, CDCl$_3$)
Compound 5-0 (400 MHz, CDCl₃)
Compound 5-1 (400 MHz, CDCl$_3$)
Compound 5-2 (400 MHz, CDCl₃)
Compound 5-2 (162 MHz, CDCl$_3$)
Compound 5-3 (400 MHz, CDCl₃)
Compound 5-4 (400 MHz, CD$_2$Cl$_2$)
Compound 5-5 (400 MHz, CD$_2$Cl$_2$)
Compound 5-6 (400 MHz, CDCl₃)
VITA

Carlos Anthony Chavez was born in 1987 in Albuquerque, New Mexico. After graduating from high school, he enrolled at the University of New Mexico in Albuquerque, New Mexico as a Biology and Chemistry double major. He began his research career in the lab of Dr. Timothy N. Lambert at Sandia National Laboratories located on Kirtland Air Force Base in Albuquerque, NM. It is at Sandia Labs that he studied synthesis and characterization of organic/inorganic hybrid materials used for energy applications. In May of 2010, he graduated with a Bachelor of Science in Biology and Bachelor of Arts in Chemistry, while simultaneously publishing numerous peer-reviewed articles at Sandia Labs (one being cited over 200 times to date). He then moved to Baton Rouge, Louisiana to attend Louisiana State University for his doctorate studies. He joined the laboratory of Professor Evgueni E. Nesterov and shortly after was awarded the National Science Foundation Graduate Research Fellowship. His research and contributions at LSU include the synthesis and development of transition metal catalysts for the polymerization of conjugated polymers. Carlos is a candidate for the Doctor of Philosophy in Organic Chemistry, which will be awarded in December 2015 with a dissertation entitled, “Development of Transition Metal Catalyzed Polymerization Reactions and Their Applications for the Preparation of Well-Defined Conjugated Polymer Architectures.”