PHOTOPHYSICS OF SINGLE CHAIN POLY(ARYLENE ETHYNYLENE)S

By

ERIC ELY SILVERMAN

A DISSERTATION PRESENTED TO THE GRADUATE SCHOOL
OF THE UNIVERSITY OF FLORIDA IN PARTIAL FULFILLMENT
OF THE REQUIREMENTS FOR THE DEGREE OF
DOCTOR OF PHILOSOPHY

UNIVERSITY OF FLORIDA

2005
For Jen.
ACKNOWLEDGMENTS

My work at the University of Florida would not have been possible without the advice, support, and friendship of the many people I have interacted with during my time here. First, I thank my advisor, Kirk Schanze. His advice, support, and seemingly unending patience have been invaluable to my achievements over the past five years.

I further acknowledge the contribution of many people who have contributed both to the work I have accomplished and to making my time in graduate school more enjoyable. Ksenija Haskins-Glusac, Boris Kristal, and Kye-Young Kim have all been both great friends and coworkers. I thank the many current and former coworkers with whom I have shared conversation and insights over the years. I would like to specifically point out Mauricio Pinto and Xiaoming Zhao for their contributions to my work. I also acknowledge the contributions of my collaborators at Brookhaven National Laboratories, John Miller and Alison Funston. More thanks are due to my friends Aleksa and Ilka Jovanavic and Cris Dancel. A special thank you goes to Janice Young.

Finally, I am grateful to my family for all of their love. My parents have offered me unending support throughout my graduate school years. I thank my grandmother for her kindness and wisdom, and also my grandfather, even though he is no longer here to share in my completion of this work. I am grateful for all of the love shared with my sisters Rochelle and Lisa. Last, I thank my brother Adam who never ceases to share his love, understanding, advice, and support.
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This dissertation presents the results of an investigation into the photophysical properties of single conjugated polymers. The study focuses on the properties of polymers as single-chain “molecular wires” rather than as bulk materials. The dissertation focuses on the design and synthesis of these materials and the use of a variety of techniques to probe their unique properties. The primary focus of the photophysical investigations is the use of optical techniques, although radiolytic techniques were also applied where appropriate.

All of the polymers under investigation were demonstrated to show rapid and efficient transport of singlet, poleron, and triplet carriers. In order to study these properties, polymers with incorporated carrier traps were synthesized. These traps were either randomly distributed throughout the polymer chain or appended to the polymers as end-caps.
Helical, organometallic polymers were also synthesized and investigated. A hydrophobic polymer with ester pendant groups was subjected to post-polymerization functionalization to give a hydrophilic material with pendant acid groups. This polymer has many similarities to DNA in that it is a polyanion that readily adopts a helical conformation characterized by face-to-face stacking of aromatic moieties. This polymer accepts many well-known DNA intercalators which show characteristic spectral changes upon binding. Additionally, binding of the polymer to a chiral guest induces the preferential formation of one of the two possible enantiomeric helices, as evidenced by circular dichroism spectroscopy.
 CHAPTER 1
INTRODUCTION

Conjugated Polymers: Background

Conjugated polymers are unsaturated materials in which the entire polymer backbone consists of atoms with a continuous $\pi$ orbital system. In 1977, it was reported that polyacetylene can exhibit significant conductivity when it is oxidized or reduced.\(^1\) The field was brought to the forefront of scientific and public attention in 2000, when the principal discoverers of this property, Heeger, MacDiarmid, and Shirakawa, were awarded the Nobel Prize in Chemistry.

From the original communication of this extraordinary property in 1977 until the present day, conjugated polymers have found a wide variety of applications, often in device fabrication. Devices as varied as light emitting diodes, light emitting electrochemical cells, plastic lasers, and thin-film transistors have featured conjugated polymers as functional components.\(^2\)-\(^9\)

A wide variety of conjugated polymer structures have been reported, and several of these are depicted in Figure 1-1. With the exception of polyacetylene, these materials feature aromatic or heteroaromatic rings that are connected either directly or via conjugated vinyl or ethynyl linkers.

Poly(phenylene vinylene) (PPV)’s, as a class, have perhaps found the most uses to date, and at least one common member of this class poly(methyl ethylhexyl phenylene vinylene), or MEH-PPV, is currently commercially available.\(^10\) The fact that PPV’s have achieved such success despite their moderate stability, cis- backbone defects, and the
rather delicate processing conditions needed in order to obtain high-quality materials, strongly suggests that investigations into other conjugated polymer architectures may allow for the fabrication of improved materials and devices.\textsuperscript{11}

![Polyacetylene, Poly(3-alkyl)thiophene, Polyaniline](image)

**Polyacetylene**  
**Poly(3-alkyl)thiophene**  
**Polarine**

![Poly-p-phenylene, Poly(phenylene vinylene), Poly(phenylene ethynylene)](image)

**Poly-p-phenylene**  
**Poly(phenylene vinylene)**  
**Poly(phenylene ethynylene)**

Figure 1-1. Examples of conjugated polymer structures.

**Poly(Phenylene Ethynylene)s**

**Applications of Poly(phenylene ethynylene)s**

One of the most promising classes of conjugated polymers is poly(arylene ethynylene)s, or PAEs. PAEs feature aromatic or heteroaromatic rings connected by ethynyl linkages.\textsuperscript{12} By far the most common type of PAEs are poly(phenylene ethynylene)s (PPEs), where the aromatic group is a benzene ring. PPEs have a tremendous advantage in that they may bear a great variety of functional group substitutents. PPEs with alkyl,\textsuperscript{13} alkoxy,\textsuperscript{14} carboxylate,\textsuperscript{15} phosphonate,\textsuperscript{16} and other pendant groups\textsuperscript{12,17} have been studied. In addition to varying the pendant group, it is possible to “dope” the polymer chains’ backbones with other moieties, including organic\textsuperscript{12,14} or metal-containing\textsuperscript{18} co-monomer units.
Recent investigations have shown that PPE’s have an astounding variety of practical uses. Many of these applications are made possible by the relative ease in which structural diversity can be built into PPE’s. For example, by incorporating pentipticyl groups into the backbone, as in Figure 1-2, Yang and Swager utilized a PPE as an effective sensor for trinitrotoluene, a common explosive.\(^{19}\)

![Figure 1-2. Schematic of Swager’s pentiptycene containing PPE, an effective TNT sensor. Picture from Swager [19].](image)

In 1998, Weder and co-workers used a PPE with a well-designed substitution pattern to fabricate a liquid crystalline display.\(^{20}\) They note that the particular PPE used in their device features an ideal set of properties for the preparation of polarized photoluminescent layers.\(^{21}\) Notably, their device shows markedly better contrast than common commercially available LCD displays, as shown in Figure 1-3.

Even more recently, PPE’s have found application in sensing biological activity. Because PPE’s are effectively chromophores wired “in series” they have the potential to act as amplifiers for chemical signaling information. Swager calls this the “molecular wire approach to signal amplification.”\(^{17}\) This approach takes advantage of the electronic communication between chromophores in a PPE.
Figure 1-3. LCD displays (A) constructed with a PPE as the luminescent layer, and (B), a commercially available display. Photograph from Weder [21].

Figure 1-4 and 1-5 are schematic diagrams explaining this effect. Figure 1-4 depicts independently functioning chemical sensors. Note that each molecule of analyte can cause a response in only one sensory molecule. The system is therefore limited by its 1:1 stoichiometry. The ability of such a system to detect, for example, a single molecule of analyte would depend on the ability to elicit a measurable response from a single receptor molecule.

Figure 1-4. Chemical sensors functioning independently. Adapted from Swager [17].

This limitation can be overcome by wiring sensors in series, as is the case of the chromophores in a PPE. In this situation, depicted in Figure 1-5, a binding event at a single receptor causes a response in every molecule in the wire. Considering that modern techniques can easily produce polymers with several hundred repeat units, this method
should be able to produce a signal amplification of two or more orders of magnitude over independently functioning receptors.

![Diagram](image)

Figure 1-5. Chemical sensors functioning in series. Adapted from Swager [17].

The Whitten lab used this effect to develop a sensor for the protein avidin. This design takes advantage of avidin’s extraordinary high binding affinity for the molecule biotin. The sensor used an anionic, water soluble PPV and a cationic quencher, methyl viologen (MV⁺), which was covalently bound to biotin. When the biotin bound quencher is introduced to a polymer solution the quencher binds to the polymer due to electrostatics, and the polymer fluorescence is quenched. Upon subsequent addition of avidin, tight binding between avidin and biotin moves the quencher away from the polymer, resulting in a strongly fluorescent polymer solution.

After this initial work with a PPV, PPEs with anionic pendant groups were used by Pinto and Schanze to develop fluorescence assays that monitor the activity of proteases in real time. The assays are somewhat alike to Whitten’s in that they depend upon the amplified quenching PPE’s by quenchers tethered to biomolecules. Figure 1-6 depicts the two types of assays developed by this approach. The first, a “turn on” assay, features a quencher bound to a positively charged “anchor” via a biomolecule tether. The polymer is initially non-emissive due to the proximity of the quencher. Enzymatic cleavage of the tether releases the quencher giving rise to the typical bright photoluminescence of the PPE. The turn off approach utilizes a “caged” quencher that is
initially insulated from the polymer backbone. Enzymatic cleavage of the “cage” leaves
the quencher in close proximity to the polymer where it effects emission quenching.

Figure 1-6. Fluorescence assays for enzyme activity using a PPE as the fluorophore.
Figure from Pinto [23].

**Synthesis of Poly(paraphenylene ethynylene)s**

The most common method of synthesizing PPE’s is the Sonogashira coupling
reaction.\(^{12,17}\) This method, involving the use of copper and palladium to couple terminal
acetylenes to aryl halides, was developed by Sonogashira in 1975.\(^{24}\) Other examples of
this transformation appeared in the literature at about the same time,\(^{25,26}\) however,
Sonogashira’s method, which requires less forcing conditions, is tolerant of a wide range
of functional groups, and does not involve preparation of copper acetylides, is the only
one that has provided access to PPE’s.
In its most common form, the Sonogashira reaction utilizes readily available bis(triphenylphosphine)palladium(II) chloride and copper (I) iodide in the presence of an amine to effect cross coupling of an aryl iodide or bromide with a terminal acetylene under anaerobic conditions. The accepted mechanism for this reaction is depicted in Figure 1-7.

When a palladium (II) catalyst is used, the initial step involves substitution of the chlorides by two terminal acetylides, followed by reductive elimination to yield the active catalyst, a palladium (0) species, and an acetylene dimer. This byproduct is not typically a problem for reactions of small molecules. However, for synthesis of polymers where exact stoichiometric balance is required, this side reaction imbalances the stoichiometry and results in reduced polymer molecular weights. Swagger suggested using a slight excess of acetylide monomer to alleviate this problem\textsuperscript{17}. However, a better solution is to substitute a palladium (0) species for the palladium (II), to circumvent the initial catalyst activation step. Tetrakis(triphenylphosphine) palladium is an excellent choice as an alternative catalyst.

The next step in the reaction is insertion of the active catalyst into the aryl-halide bond, followed by transmetallation of the halide by a Cu (I) acetylide. Reductive elimination of the aryl acetylide product regenerates the catalyst. In order to prevent the formation of an inactive complex between palladium and oxygen, the reaction is completed under anaerobic conditions.

The reactivity of aryl halides in Sonogashira conditions depends on the aryl-halide bond dissociation energy. Thus, in general, aryl iodides are more reactive than aryl bromides, and aryl chlorides are typically unreactive. The difference between the
reactivity of iodides and bromides is sufficiently great that aryl iodides are known to undergo reaction to the nearly complete exclusion of a competing reaction with aryl bromides.\(^{27}\) In addition, reactivity of aryl iodides is typically fast even at room temperature, while aryl bromides often require higher temperatures and longer reaction times.

![Mechanism of the Sonogashira Reaction](image)

Figure 1-7. Mechanism of the Sonogashira Reaction.

Recent advances in catalysis have made possible the use of aqueous conditions and inorganic bases,\(^{28}\) the use of aerobic conditions without copper,\(^{29}\) and coupling to alkyl chlorides.\(^{30}\) However, because these methodologies require the use of harsh conditions, catalysts that are not readily available, or both, they are not often used to access PPE’s.
Molybdenum and tungsten based catalysts have also been used to synthesize PPE’s by alkyne metathesis reactions. This methodology, developed primarily in the Bunz and Moore laboratories, was the subject of a review article in 2001. Bunz coined the term acyclic diyne metathesis (ADIMET) to describe this condensation polymerization, which formally condenses a molecule of hydrogen while forming a new bond between two terminal acetylenes.

The ADIMET methodology addresses some of the problems associated with Sonogashira polymerizations, including ill-defined endgroups due to dehalogenation and phosphonium salt formation, and the difficulty in producing very high molecular weight materials. In addition, ADIMET polymerizations require only a single type of functional group, thus eliminating the several practical difficulties. Specifically, the problems associated with the strict stoichiometric balance required for two component A-A, B-B type Sonogashira polymerizations between aryl diiodides and aryl diethynes, or the synthetic difficulties often associated with the synthesis of ultra-high purity A-B type iodo-ethynyl substituted arenas.

In its earliest incarnations, ADIMET had several major drawbacks. These include the need for harsh conditions, and intolerance of a wide degree of functionality. However, more recently, the Moore group developed a simple synthesis of a molybdenum alkylidine catalyst that shows good activity in ADIMET under reasonable reaction conditions. This catalyst also shows improved functional group tolerance, and yields higher molecular weight polymers than the Sonogashira methodology. Despite these improvements, ADIMET remains the less popular of the two methods, probably because the effective ADIMET catalysts are not commercially available, whereas the
palladium catalysts used for Sonogashira polymerizations can be purchased relatively inexpensively.

**Platinum Containing Poly(phenylene ethynylene)s: Platinum Polyynes**

Another significant class of PPEs are those which contain platinum in the polymer backbone. These materials are of particular interest because their photophysics are dominated by long lived, phosphorescent $^3\pi,\pi^*$ excited states.$^{35-39}$ This property makes them useful candidate materials for the fabrication of electroluminescent devices,$^{39,40}$ and for applications in optical limiting.$^{41}$

The general structure of a platinum containing PPE is depicted in Figure 1-8. These materials consist of sp hybridized alkyne carbons linking bis(trialkylphosphine)platinum (II) to phenylene rings. When the aromatic rings are not substituted, good solubility in organic solvents can be achieved by using butyl or longer alkyl groups.

![Figure 1-8. General structure of a platinum containing PPE.](image)

Platinum containing PPE’s are synthesized utilizing the Hagihara coupling reaction, which was discovered in 1978.$^{42}$ The reaction involves the Cu (I) catalyzed substitution of chlorine on a bis(trialkylphosphine)platinum (II) chloride in the presence of an amine. Although the platinum chloride may be present as a mixture of *cis* and *trans* isomers its stereochemistry is in practice irrelevant, because the *cis* complex rapidly isomerizes to *trans* in the presence of a secondary or tertiary amine.
The amine serves to deprotonate the acetylene, which presumably forms a copper acetylide upon reaction with the catalyst. The activated acetylide then substitutes chloride forming the platinum-carbon bond. The reaction can also be carried out in the absence of catalyst, but under these conditions the product is only mono-substituted, with one chloride ligand remaining on the platinum. The catalyst-free variation is therefore not useful for making polymers, but it has proved useful in the synthesis of oligomeric platinum containing PPEs.

![Figure 1-9](image.png)

**Figure 1-9.** Absorption (a) and emission (b) spectra of oligo platinum PPEs with increasing chain length. In the emission spectra, fluorescence is denoted by F and phosphorescence is denoted by P. Note that the fluorescence intensity scale is magnified 100x with respect to phosphorescence. Figure from Liu [44].

Interestingly, several studies have shown that conjugation through the metal center in platinum containing PPE’s is not efficient, and therefore these materials have a rather low conjugation length. For example, Beljonne used calculations to conclude that the triplet state of platinum containing PAE’s in general is spatially confined. Later, Liu and coworkers synthesized a series of monodisperse oligo-Pt PPEs and studied their photophysical characteristics. The absorption and emission spectra of these polymers, reprinted in Figure 1-9, are quite informative. The increase in molar absorbivity and red-
shift in the fluorescence with increasing chain length indicate that the singlet ground state and first singlet excited state are delocalized across the oligomers. However, the invariance of the phosphorescence with respect to increasing chain length indicates that the triplet state in platinum PPEs is spatially confined over a relatively small distance of about five monomer units.

**Meta Linked Poly(phenylene ethynylene)**

While poly(*para* phenylene ethynylene)s have been known for some time, it was not until 1997 that Lavastre and co-workers reported a method to efficiently access their *ortho* and *meta* analogues.46 Soon after, researchers in Moore’s group reported that oligo(*meta* phenylene ethynylene)s have the ability to undergo dramatic conformational self assembly in solution.47,48 Moore’s oligomers, featuring a solubulizing oligo(ethylene oxide)ester pendant group, are depicted in Figure 1-10.

When they are of sufficient length, Moore’s phenylene ethynylene oligomers have the ability to adopt a helical tertiary structure. This conformational effect is largely solvent dependant. In methylene chloride, the oligomers are well-solvated, and exist as a random coil. In acetonitrile, however, the oligomers fold into a helical conformation. This change can be monitored by using absorption and emission spectroscopy in solvents of different composition. Specifically, an increase in the mole fraction of acetonitrile in
the solvent results in a hypochromic effect in the absorption, with a good isobestic point. Also, eximer-like fluorescence is observed in with increasing amounts of acetonirile in the solvent. These results imply a cooperative transition.

Later, Tan and coworkers used a PPE with sulfonate pendant groups and a meta-para linkage pattern to study these conformational changes in water. They found that the polymer they studied was well solvated by methanol and poorly solvated by water. This polymer exhibited properties quite similar to that of Moore’s oligomers when the composition of the solvent was varied from pure methanol to pure water. The conformation changes in this polymer are depicted in Figure 1-11.

![Figure 1-11. A segment of the meta-para PPE used by Tan adopts a random coil conformation in methanol (left), and a helical conformation in water (right). The side chains have been left off for ease of viewing.](image)

More recently, the Tew laboratory studied polymeric *meta* phenylene ethynylenes (*m*-PPEs). These studies compared poly electrolytes with and without bulky side groups. Their studies showed that if, for steric reasons, a large pendant group must orient itself inside of the helix, then self-assembly is restricted even in the presence of a poor solvent.

Additionally, the cavity inside the helix of *m*-PPEs can be used to bind guest molecules. For example Moore’s group used an oligo *m*-PPE to bind a chiral
monoterpene guest.\textsuperscript{52} This guest induces chirality in the helical conformation of the \textit{m}-PPE oligomer, and results in a circular dichroism (CD) signal. The induced chirality originates from a preferential binding of one enantiomer of the helix to the guest, and is made possible because the association constant between the chiral guest and the polymer is different for each of the enantiomeric helices. This process is depicted in Figure 1-12.

Figure 1-12. Chiral induction in a helical polymer by preferential binding to a chiral guest.

Meta-PPEs may have other interactions with small molecules besides this host-guest chemistry. For example, Tan’s polymer, described earlier, is physically similar to DNA in that it adopts a helical conformation with face-to-face stacking of aromatic rings. These similarities allow it to bind to molecules in a fashion similar to DNA. An example is binding to the complex Ru(bpy)\textsubscript{2}(dppz), where bpy is 2,2’ bipyridine and dppz is dipyrido[3,2-a:2’,3’-c]phenazine. In a solution of pure water, Ru(bpy)\textsubscript{2}(dppz) is non emissive because hydrogen bonding between the phenazine ligands and the solvent allow the emission to couple to the vibrational modes of water and effectively quench the compound’s luminescence.\textsuperscript{53} However, upon intercalation into DNA, Ru(bpy)\textsubscript{2}(dppz) is “shielded” from this solvent interaction and becomes strongly luminescent.\textsuperscript{53,54} This
phenomenon is often known as the “light stick effect”. That this effect is also observed when Tan’s polymer, in its helical conformation, is added to a solution of Ru(bpy)$_2$(dppz) strongly suggests that the metal complex intercalates into the polymer.

**Conjugated Polymers as Molecular Wires**

**Single Chain Conjugated Polymers**

Much of the recent interest in conjugated polymers stems from their potential applications in electronic, electro-optical and optical devices.$^{55}$ One major factor which makes conjugated polymers excellent candidates for these applications is that they provide exceptional transport properties for charges and excitons. As such, a great deal of effort has been expended to understand the carrier transport properties of these materials.

The vast majority of the work in this area has focused on bulk properties of the polymers in films.$^{37,56-59}$ This is understandable, as there is a significant interest in using polymer films as active layers in optio-electronics.$^{60}$ These investigations have offered considerable insight into structure-property relationships of polymers in bulk.

However, there is another paradigm for exploiting the intriguing properties of conjugated polymers. It is also conceived that these materials may serve as transport materials as single-chain “molecular wires.” The molecular wire concept entails single molecules acting as carriers in one-dimension only. Thus, a molecular wire would have to have an appropriate molecular geometry and be able to adopt a predictable conformation in addition to having excellent transport properties along its long axis. In addition to the requirements that they be excellent charge carriers over long distances, the energetics of a good molecular wire must not vary drastically with length.$^{61}$
Several examples of conjugated oligomers or polymers being used as molecular wires are known. For instance, in 2000, Tour attached a linear terphenyl to gold electrodes by using thiol substituents as “alligator clips.” Upon applying a potential difference across the electrodes, the terphenyl undergoes a conformational change and completes the circuit between the electrodes with a measurable conductivity and resistivity. This experiment is depicted in Figure 1-13.

![Figure 1-13. A conjugated oligomer in use as a molecular wire. Figure adapted from Tour [62].](image)

The study of molecular wires is particularly important in the context of nano-scale electronic devices, where it is envisioned that the charge or exciton carriers will be single polymer or oligomer chains. Many conjugated polymers, especially poly(para-arylene ethynylene)s (PAEs) fit the requirements for molecular wires. First, PAE’s are locked in a linear geometry along the direction of conjugation. Second, although the primary mode of transport through PPE’s in the solid state is inter-chain hopping, the extended conjugation in these materials seems intuitively ideal for intra-chain transport properties along the direction of conjugation.
Indeed, there has been a great deal of recent interest in studying the transport of excitons along single chain conjugated polymers. This is somewhat of a challenge, because PPE’s are known to aggregate in solution, and the photophysics of the aggregates are differ significantly from that of single-chain polymers. The most common approach to these investigations is to study the polymers in dilute solutions, where interchain interactions are minimized.

Several techniques have been used to explore exciton transport in conjugated polymers. One method uses co-polymerization to incorporate low-energy trap sites for excitons in the polymer chain. For example, Swager, Gil, and Wrighton synthesized a PPE end-capped with anthracene linked through the 9-position, as shown in Figure 1-14. Upon photoexcitation of the polymer main chain, the emission of the polymer is quenched and replaced with anthracene fluorescence.

Alternatively, the polymer may be used to bind a small molecule quencher, which serves to accept either energy or an electron from the excited state of the polymer. In one particularly intriguing study, Wang and Wasielewski used the PPV derivative in Figure 1-15, which features pyridine comonomers in the main-chain, to bind metal ions. Upon binding, metal ions such as Ni$^{2+}$, Cu$^{2+}$, and Mn$^{2+}$ effectively quench the polymer emission. This effect is not observed with a physical mixture of a pristine polymer...
(without bipyridine) and bipyridine. The highly effective quenching indicates that the exciton created by initial photoexcitation diffuses rapidly to the metal trap site.

![Figure 1-15. A metal binding conjugated polymer. Figure adapted from Wang [62].](image)

In related studies, cyclophane monomers have been used to bind viologen quenchers,\textsuperscript{70-72} and ionic side chains have been used to bind oppositely charged metals and molecular ion traps.\textsuperscript{72-76} All of these studies demonstrate that energy transfer in single chain conjugated polymers is extremely rapid and highly efficient.

**Charge Transport**

Charge or electron transport (ET) in solution can typically be viewed as an interaction between an electron donor (D) linked to an electron acceptor (A) through some bridging species (B).\textsuperscript{77} This DBA scheme is understood fairly well when the bridge is molecular.\textsuperscript{78-80} Indeed, detailed comparisons between theoretical and experimental results have been essential in unifying this field.\textsuperscript{80} In this work, the gap between the donor-HOMO and bridge-LUMO for a variety of systems was tabulated.

In general, there are two mechanisms for ET in DBA systems. Superexchange is observed when ET occurs by a tunneling process and the electron never resides on the
Alternatively, charge transport may proceed by a hopping mechanism via oxidation or reduction of the bridge by the donor, followed by ET from the bridge to the acceptor. These two processes may both be operative in the same system, as per equation 1-1, where $k_{\text{tun}}$ is the rate of ET by superexchange and $k_{\text{hop}}$ is the rate of ET by hopping.

$$k_{\text{ET}} = k_{\text{tun}} + k_{\text{hop}} \quad \text{(1-1)}$$

In conjugated polymers, as in typical molecular systems, the superexchange model is expected to be highly dependent on the length of the polymer. The dependence of the rate of superexchange on the degree of polymerization ($D_p$) is expressed by equation 1-2.

$$k_{\text{ET}} = k_{\text{tun}} = k_0 \exp(-\beta D_p) \quad \text{(1-2)}$$

In this equation, $\exists_N$ is dependent on the length of the monomeric unit (which, in the case of PAE’s, may contain one, two, or more aromatic rings), and the natural logarithm of the ratio of the coupling energy between the monomeric units, $H_{BB}$, and the energy gap between the initial state (DBA) and the mediating state, $\Delta E_{DB}$. The mediating state is $D^+B^{-}A$ for electron transport, or $DB^+A^-$ for hole transport. Therefore it follows that a small value of $\beta$ is desirable for long-range ET, thus pointing to the desire to minimize the energy of the mediating state. It is important to note that in the superexchange mechanism the mediating state is only a virtual state, and that the electron or hole never actually resides on the bridge.

In the hopping mechanism, the mediating states are real, and the bridge is oxidized and then reduced (or reduced and then oxidized) during the ET process. The rate of this process is Ohmic, that is, it is inversely proportional to the distance between D and A.
In the case of a conjugated polymer, this means that as $D_p$ increases, the rate of charge transport by hopping should decrease.

Several interesting phenomena are predicted when both mechanisms are applied in parallel. One particularly interesting result of the mathematics is a phenomenon known as resonant tunneling, which occurs when the energy gap is zero. In this scheme, the overall rate of ET should not vary greatly with increasing $D_p$.\textsuperscript{84}

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Figure 1-16. MEH-PPV with saturated conjugation breaks.

ET theory therefore indicates that understanding the nature of the oxidized or reduced state of conjugated polymers is of key importance, since the energetics of the charged state and the diffusiveness of the charge are key factors in explaining the transport abilities of conjugated polymers used as molecular wires. A study by Candeias and coworkers was the first to provide this information. Candeias examined a series of MEH-PPV derivatives in which varying amounts of the vinyl linkages had been hydrogenated, as in Figure 1-16.\textsuperscript{65} The hydrogenated olefins effectively break the conjugation in the polymer backbone.

Pulse radiolysis was used to perform a one-electron oxidation on the conjugated polymer backbone, and the energy of the polymer cation radical was measured by absorption spectroscopy. The study showed that breaks in the conjugation length
increase the energy of the cation radical, thus unambiguously demonstrating that the charged species is stabilized by conjugation through the polymer chain.

**Charge Injection**

In Candeias’s work and in some of the work described in this dissertation, charge is injected into a conjugated polymer by producing a solvated hole or electron which migrates to the analyte. This process can be modeled using existing theory, and understanding this theory is a useful precursor to the studies presented herein.

Theory has provided solutions to the problem of a mobile point charge diffusing to a number of spherical monomer units joined together in a one, two or three dimensional array. The solution for a one dimensional array is an appropriate model for PAEs, which are essentially one dimensional rigid rods. Traytak’s solution and its recent test by Grozema employ an effective radius, $R_{\text{eff}}$ defined in terms of the reaction radius $R_m$, for one monomer unit and the number of units in the polymer chain, $n$, as in equation 1-3.

$$R_{\text{eff}} = \frac{nR_m}{1 + \frac{R_m}{a} \ln(n)} \quad (1-3)$$

The diffusion-controlled rate of reaction with a chain of length $n$, is then given by equation 1-4, which is identical to Smoluchowski’s classic solution for a reaction of spherical particles where $D$ is the sum of the diffusion coefficients of the reactants.

$$k(t) = 4\pi R_{\text{eff}} D (1 + R_{\text{eff}}/(\pi Dt)^{1/2}) \quad (1-4)$$

The second term in equation 1-4 is often called the transient term, and contributes less than 10% to the overall rate when larger than $10R^2/\pi D$. For small species that diffuse rapidly in solution, this time is generally less than a few nanoseconds. However,
Grozema showed that large polymers have much larger effective radii and consequently a much larger and long-lived transient term. While the steady-state, diffusion controlled rate constant per repeat unit falls with increasing degree of polymerization, some of that loss is recovered by the larger transient term.\(^85,86\) Thus, the bimolecular rate constant for transfer of a solvated electron \((e^-)\) or hole \((h^+)\) to a PPE will initially decrease with an increasing chain length and then, after reaching a minimum, increase again.

**Description of the Present Study**

The present study aims to gain an increased understanding of the properties of single chain PPEs. Careful design and synthesis of polymers with appropriate charge or energy traps, or with the capability to undergo predictable conformational changes, is the primary means to these goals. Well-designed polymers allow for the monitoring of specific spectral changes associated with the injection of energy or charge, or those associated with conformational changes, thus making it possible to gain an increased understanding of these properties.

The experiments described in this dissertation were performed in dilute solution, except for a few cases where higher concentrations or films were used in order to demonstrate the differences between single-chain and aggregated or bulk PPEs. Although modern microscopic methods allow for the collection of a variety of photophysical data on single-chain conjugated polymers in the solid state, there are severe practical difficulties in performing many of the time-resolved experiments described in this study under those conditions.

Chapter 2 of this dissertation is concerned primarily with charge transport in PPEs. PPEs with two different molecular architectures were synthesized both in their pristine
form and with low oxidation potential moieties affixed to the termini. These traps were
designed to act as low-energy traps for cation radicals (holes) in the polymer backbone.

The unique laser electron accelerator facility (LEAF) at Brookhaven National
Laboratories was employed to inject charges into the polymers and measure their
spectroscopy in a time-resolved fashion. By carefully choosing a trap that exhibits
spectral characteristics that are different from those of the parent polymer, it was hoped
that the dynamics of charge migration in PPEs could be measured quantitatively.
Although the limits of even the most modern instrumentation prevent quantitative
measurement of these rates, this system enabled many other useful spectral and
thermodynamic properties of a charged PPE to be elucidated.

Chapters 3 and 4 deal with platinum containing PPEs. Chapter 3 describes the
synthesis and characterization of a series of platinum containing PPEs where low energy
 traps are incorporated into the main chain. The trap concentration was varied throughout
the series. These materials were used to gain insight into the mechanism of energy
transport in platinum containing PPEs. Use of a variety of steady-state and time-resolved
methods reveal that although the photophysics of platinum containing PPEs are
dominated by their long-lived triplet states, the results in this chapter show that their short
and often optically inactive singlet excited states do play an important in inter-chain
charge transport.

Chapter 4 deals with a platinum containing PPE that is linked through the *meta*
position. This polymer is able to self-assemble into a helical conformation that accepts
guest molecules, much in the way that organic *m*-PPEs or DNA do. This work represents
the first careful study of a water soluble organometallic polymer that undergoes these types of conformational changes.
CHAPTER 2
RADICAL TRANSPORT IN END-CAPPED POLY(ARYLENE ETHYNYLENE)S

Introduction

Very little effort has been made to examine the transport of charges (radical cation or radical anions) in single chain poly(arylene ethynylene)s, or to understand the spectroscopy or thermodynamics of these charged species. This is unfortunate, because charged single chain conjugated polymers are envisioned to be the active species in a variety of applications, especially molecular electronics. In fact, a need to develop further understanding into the nature of charged states in conjugated polymers was recently highlighted by several senior researchers in the field. The work presented in this chapter is an important step towards fulfilling this need.

Pulse radiolysis experiments were used to investigate the transport dynamics of radical cations (holes) in single chain conjugated polymers. This problem was approached by using conjugated polymers that are end-capped with functional groups that serve as traps for radical cations generated on the main polymer chain. The conditions for an end-cap to serve as a trap is the end-cap have a lower oxidation potential than that of the main chain, that is, $E_{ox}^0(T) < E_{ox}^0$ (polymer), where T represents the radical cation trapping moiety. In this chapter, the results of a study using poly(arylene ethynylene)’s with 2,2’:5’,2’’ terthiophene ($T_3$) end-caps is reported. PAE’s were chosen because they posses a linear “molecular wire” structure, and are easily synthesized via Pd mediated Sonogashira condensation polymerizations. $T_3$ was chosen as an end-cap because it was anticipated to meet the requirements for a radical cation
trap, eg. $E_{\alpha}^0 (T_3) < E_{\alpha}^0 (\text{polymer})$. In addition, the spectroscopy of oligothiophene cation radicals has been investigated extensively, and it was therefore anticipated that it would be possible to distinguish between a cation radical localized on the end-group (ie. $T_3^+$) from a polymer-based cation radical (ie. PAE$^+$).

The objectives of this study are two-fold. The first objective is to study experimentally the spectroscopic properties of charged single-chain PAE’s. The second is to determine the rate of hole transfer ($k_{HT}$) for a radical cation localized on a the polymer main chain to the end-cap, as in equation 2-1.

$$h^+ \quad k_{HT} \quad T_3-(PAE)-T_3 \rightarrow T_3-(PAE^*)-T_3 \rightarrow T_3-(PAE)-T_3^* \quad (2-1)$$

**Results and Discussion**

**Synthesis and Structural Characterization of Poly(arylene ethynene)s**

The chemical structures and acronyms for the polymers featured in this study are shown in Figure 2-1. The numerical subscript in each polymer’s name represents the number average degree of polymerization, $\overline{X}_n$, as calculated from the GPC derived number average molecular weight, $M_n$. For the end-capped polymers, $\overline{X}_n$ includes only the units of the polymer main chain and *not* the end-groups. Furthermore, it is important to note that PPE type polymers contain two phenylene rings per repeat unit while PBpE type polymers contain three phenylene rings per repeat unit.

In addition to the polymers, the model compound Ph-T$_3$ was synthesized by coupling 2-terthophene and $p$-iodo toluene. This compound was designed to model the
end-capped termini of the polymers. The synthesis of the polymers and monomers used in this study is outlined in Figure 2-2.

Figure 2-1. Structures of the polymers and model compounds used in this study.

The monomers used in these polymerizations, 2,5-bis(2-ethylhexyl)-1,4-diiodo-benzene and 1,4-diethynyl benzene, and 4, 4’-diethynyl biphenyl were synthesized by modified literature procedures. In particular, the synthesis of the diiodo monomer was substantially improved. Diiodination of 1,4 dimethoxybenzene was accomplished with one equivalent of molecular iodine and 0.7 equivalents of potassium periodate in refluxing acidic media. Using this ratio of reagents affords substantially better yields (85-90%) than use of an excess of iodine and potassium periodate (about 40% in our hands). Additionally, since iodine is present in a stoichiometric amount, the reaction can be monitored by watching for the disappearance of the dark-brown iodine color. It is important to note that iodine may sublime in the condenser during the reaction, and it must occasionally be pushed back into the reaction mixture using a glass rod to prevent
clogging. If the condenser becomes completely clogged, the build up of pressure may result in an explosion. Addition of a small amount of chloroform to the reaction mixture can help minimize this problem, but may reduce the yield somewhat.

Figure 2-2. Synthesis of polymers and model compounds used in this study.
Demethylation of the alkoxy groups was preformed using boron tribromide in dry dichloromethane under anaerobic conditions. The resulting hydroquinone is recovered by evaporation of most of the solvent, and precipitation from methanol-water. Upon workup of this reaction, it is important to add a few spatula tips of sodium sulfite (Na₂SO₃) to prevent air-oxidation of the hydroquinone in solution. The hydroquinone was then alkylated using 1-bromo-2-ethyl hexane in refluxing methyl ethyl ketone with potassium carbonate under anaerobic conditions. Again, addition of sodium sulfite upon workup is important to prevent oxidation of the product upon exposure to air in a basic medium. The monomer is obtained as a colorless liquid.

In an effort to bypass the use of boron tribromide, which is both expensive and highly toxic, another synthesis of this monomer was attempted. In this effort, hydroquinone was first alkylated with 1-bromo-2-ethyl hexane and then iodinated as described above. However, the monomer resulting from this synthetic sequence is a red-brown oil, instead of the colorless liquid obtained by the original synthesis. The color, likely due to complexation of the product with trace amounts of iodine, cannot be removed by treatment with activated carbon or by column chromatography. It is probable that, in the original synthetic sequence, any remaining traces of iodine are removed by recrystallization of the intermediates (both 2,5-diiodo-1,4-dimethoxybenzene and 2,5-diiodo-1,4-dihydroquinone are highly crystalline). However, there are no crystalline intermediates in this alternate synthesis. Importantly, use of the colored monomer (from the alternate synthesis) in polymerizations gives only low molecular weight polymer, even under optimized polymerization conditions. Thus, this synthesis is
not a suitable method to produce the high-quality monomer needed for successful polymerizations.

The alkoxy side groups are used to help impart solubility on the final polymers. A racemate of the chiral 2-ethylhexyl group was chosen because this group gives a mixture of stereoisomers in the resulting monomer. Specifically, the di-iodo monomer is present in the polymer as a pair of diasteromers, one of which is \textit{meso}, and the other which exists as a pair of enantiomers. The resulting stereo-irregularity in the polymer backbone was designed to discourage inter-chain aggregation and improve solubility of the polymers. In fact, the biphenylene based polymers, with and without end-caps, proved to be quite soluble in many common organic solvents, including THF, chloroform, and dichloromethane. The phenylene based polymers also exhibited good solubility in these solvents, however, upon complete evaporation of solvent the phenylene based polymer forms a film which does not completely redissolve even after several days of continued stirring and gentle heating. Thus, in order to obtain the $^1$H NMR spectrum of this polymer, it was necessary to dissolve it in a mixture of dichloromethane, acetone, and hexanes. Because hexanes and acetone are poor solvents for this polymer, the film formed by evaporation of this polymer solution can be redissolved in a deuterated solvent. However, even using this method, if the solvent is completely removed the film becomes insoluble. Therefore the NMR, shown in Figure 2-3, is partially obscured by solvent peaks.

These problems made it desirable to find an alternative to the 2-ethylhexyloxy side group that would show improved solubility characteristics. Use of the undecyloxy side group alleviated many of the problems, and allowed a simpler synthesis. It was
expected that 2,5-diundecyloxy-1,4-diiodobenzene would be crystalline, and it was therefore hoped that the alternate synthesis that failed to produce useful monomer with 2-ethylhexyloxy side chains would be useful. Indeed, alkylation of hydroquinone with 1-bromoundecane followed by iodination as described above yields a product that can be easily purified by recrystalization from methanol-water giving a white solid that can be used to make reasonable molecular weight polymers.

The films that result from evaporation of solutions of the phenylene-based polymers are somewhat more soluble than those from similar polymers with the 2-ethylhexyloxy side group, and it is possible to obtain proton NMR spectra that clearly show the end-group protons. Figure 2-4 shows the $^1$H NMR spectra of the phenylene based polymer with undecyloxy side groups. Figure 2-5 is an expansion of the aromatic region of the phenylene polymer with undecyloxy side groups which has been scaled to clearly show the thienyl protons. The doublet at 7.19 ppm integrates to one relative to the other thiophene protons, and can be assigned to the proton in the 5 position on the terminal thiophene. Three multiplets at 6.84, 7.11, and 7.66 ppm each integrate to two, and each is assigned to the pairs of protons in the 3 and 4 positions on each of the respective thiophene rings. Despite the somewhat improved physical properties of the polymers resulting from 2,5-diundecyloxy-1,4-diiodobenzene, all of the photophysical and radiolytic experiments described here were performed on the polymers shown in Figure 2-1, which feature 2-ethylhexyloxy side groups, and all discussion henceforth will refer to those polymers unless specifically noted.
Figure 2-3. NMR of T₃PPE₁₃ with 2-ethylhexyloxy side groups.

Figure 2-4. NMR of T₃ end-capped PPE with undecyloxy side groups.
The final polymers were synthesized by AA, BB condensation polymerizations of aryl iodides and aryl ethynlenes using the Sonogashira reaction.\textsuperscript{12,17,66,69} For the polymers without end-caps (the “parent” polymers) an equimolar ratio of aryl iodide to aryl ethynylene groups were used in the polymerizations. For the synthesis of T$_3$PPE\textsubscript{13} numerous experiments were conducted to determine the optimal stoichiometry for end-capping, and the results are outlined in Table 2-1. In this table, I-Ar-I refers to 2,5-diundecyloxy-1,4-diiodo benzene. These experiments indicated that a small excess of iodine functionality was required to give moderate $M_n$ values. Additional experiments using the optimized ratio of end-cap to diiodo arene in which the reaction time was varied showed little change in the Mn of the resulting polymer for reaction times of sixteen hours or longer.
Table 2-1. Conditions used in end-capping polymerizations.

<table>
<thead>
<tr>
<th>Trial</th>
<th>Equivalents</th>
<th>Time/hrs</th>
<th>Mn</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$T_3$-I-Ar-I</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>1</td>
<td>99</td>
<td>12</td>
</tr>
<tr>
<td>2</td>
<td>5</td>
<td>95</td>
<td>12</td>
</tr>
<tr>
<td>3</td>
<td>10</td>
<td>90</td>
<td>12</td>
</tr>
<tr>
<td>4</td>
<td>5</td>
<td>95</td>
<td>10</td>
</tr>
<tr>
<td>5</td>
<td>5</td>
<td>95</td>
<td>24</td>
</tr>
<tr>
<td>6</td>
<td>5</td>
<td>95</td>
<td>48</td>
</tr>
<tr>
<td>7</td>
<td>10</td>
<td>100</td>
<td>16</td>
</tr>
</tbody>
</table>

a – all trials used 100 equivalents of the diethynyl monomer.

b – The $M_n$ is reported from GPC relative to polystyrene standards.

Each of the polymers was analyzed by gel permeation chromatography relative to polystyrene standards, and $^1$H NMR spectroscopy. $^{13}$C NMR was not performed because of the solubility limits of the polymers. Even in the ethylhexyloxy substituted polymers, which are not completely free of solvent, NMR can be used to give an independent estimation of $\bar{X}_n$ in the end-capped polymers. In order to estimate the degree of polymerization, it is useful to take advantage of a stoichiometric imbalance of the monomers due to end-capping. Careful inspection of the structure of the end-capped polymers reveals that the ratio of phenylene (or biphenylene) to dialkoxyphenylene monomers is $(n+1):n$, where $n$ is the chain length. By comparing the peak ratios of the phenylene (or biphenylene) and alkoxyphenylene monomers it is thus possible to calculate $\bar{X}_n = 7$ for $T_3$PPE, and $\bar{X}_n = 8$ for $T_3$BpPE. These NMR derived values are somewhat smaller than those derived from GPC, which is consistent with accepted notion that GPC, especially relative to standard “random coil” polymers, tends to exaggerate the $\bar{X}_n$ of conjugated rigid-rod polymers. $^{13,88,89}$ Regardless of these difficulties, GPC remains the most common method for determining the molecular weights of conjugated polymers, and polystyrene or other random coil polymers are the most commonly used standards.
Absorption and Fluorescence Spectroscopy

Phenylene based polymers

The UV/visible absorption spectra of PPE$_{164}$, T$_3$PPE$_{13}$, T$_3$, and PhT$_3$ are shown in Figure 2-6. The spectra of PPE$_{24}$ are identical to those of the longer molecular weight sample, and are therefore excluded. Molar absorptivity and selected fluorescence lifetime data is provided in Table 2-2.

The absorption and emission spectra of the parent polymers are alike to those of other, structurally similar PPE’s. $^{12,66,90}$ The absorption spectra are dominated by the allowed, long-axis polarized $\pi \rightarrow \pi^*$ transition, while the fluorescence features a sharp, narrow band which is dominated by the zero phonon transition.

The absorption spectrum of T$_3$PPE$_{13}$ is quite similar to that of the parent PPE$_{164}$, except for the presence of a long wavelength tail (note arrow in Figure 2-5), which correlates to a low-energy moiety in the end-capped polymer, presumably the T$_3$ end-cap. The small intensity of this tail is unsurprising, considering that the end-caps are present at very low concentration compared with the main chain of the polymers.

Table 2-2. Selected photophysical data for PAE’s

<table>
<thead>
<tr>
<th>Polymer</th>
<th>$\lambda_{\text{max}}^{\text{abs}}$ / nm</th>
<th>$\varepsilon_{\text{max}}$ / $M^{-1}\text{cm}^{-1}$</th>
<th>$\lambda_{\text{max}}^{\text{flr}}$ / nm</th>
<th>$\phi_{\text{em}}^{\text{flr}}$</th>
<th>$\tau_{\alpha}$ / ns ((\alpha))$^a$</th>
<th>$\tau_{\eta}$ / ns ((\alpha))$^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>PPE$_{164}$</td>
<td>411</td>
<td>$5.6 \times 10^4$</td>
<td>452</td>
<td>0.33</td>
<td>0.5 (0.97)</td>
<td>0.6 (0.80)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>3.9 (0.03)</td>
<td>2.5 (0.20)</td>
</tr>
<tr>
<td>T$<em>3$PPE$</em>{13}$</td>
<td>414</td>
<td>$6.5 \times 10^4$</td>
<td>453, 496</td>
<td>0.44</td>
<td>0.5 (0.94)</td>
<td>0.6 (0.89)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>3.4 (0.06)</td>
<td>3.2 (0.11)</td>
</tr>
</tbody>
</table>

$^a$ Fluorescence decay lifetimes from biexponential fits. $\tau$ and $\alpha$ values are, respectively, the lifetimes and normalized amplitudes of the individual decay components.
The difference in fluorescence between the parent and end-capped polymers is quite noticeable, even upon simple examination by eye. Upon irradiation with long-wavelength ultraviolet light, the parent polymer emits a bright blue fluorescence, while the fluorescence of the end-capped polymer appears green. Initial examination of the data suggest that the fluorescence of T₃PPE₁₃ is a combination of emission from two different excitons: one on the polymer main-chain (PPE*-T₃), and one localized on the T₃ end-group (PPE-T₃*). However, examination of the small molecule models shows that the situation is actually much more complex. The absorption and fluorescence of T₃ is considerably blue-shifted from that of both PPE₁₆₄ and T₃PPE₁₃. This is a clear indicator that an excited state localized on T₃ is at a significantly higher energy than the PPE*
exciton. A clearer understanding can be gained by noting that the absorption and fluorescence of Ph-T₃ is significantly red-shifted from that of T₃, indicating that there is a substantial delocalization of the T₃ excited state into the adjacent phenylene unit. Indeed, excited state molecular orbital calculations (outlined below) clearly indicate that although both the HOMO and LUMO are mostly localized on the T₃ end-cap, orbital mixing between the end-cap and the polymer main-chain extends the conjugation through several phenylene rings. Thus, the spectra of T₃PPE₁₃ derives from an excited state that is mostly contained on the T₃ end-cap, with some contribution from the neighboring phenylenes in the chain. The fact that the excited state of T₃PPE₁₃ is a composite of phenylene and thiophene mixing is supported by the fact that the fluorescence T₃PPE₁₃ is independent of excitation wavelength, even when the excitation is at the long-wavelength “tail” of the absorption which is due primarily to the end-caps. It is also important to recognize that these results are also not consistent with a physical mixture of end-capped and non-end-capped polymers, thus lending additional support to the structural characterization of the polymers.

The notion that there is considerable mixing between the end-cap and the polymer main chain is also supported by fluorescence lifetime measurements (Table 2-2). The decay profiles of PPE₁₆₄ and T₃PPE₁₃ are quite similar. Both are dominated by a very fast (τ ≈ 0.5 ns) component. Furthermore, the emission lifetimes are wavelength independent, even when measured in the “green” band associated with the end-cap. The fast decay of PAE’s is largely associated with their extended conjugation. The fast, wavelength independent decay of T₃PPE₁₃ thus supports the idea that the end-cap is significantly delocalized into the polymer chain. If this were not the case, the decay
profile of T₃PPE₁₃ would be expected to vary significantly with wavelength; the long-wavelength emission, if it were due to a moiety with only a small degree of delocalization, (ie. T₃, with only three aryl rings) would be expected to exhibit a much slower decay than the emission associated with the polymer main-chain which contains an average of 26 aryl rings.

The spectroscopic behavior of the T₃ end-capped polymers present some contrast to previous work where a structurally similar PPE was end-capped with anthracene linked through the 9-position. In the 9-anthracenyl end-capped polymer, the PPE-based fluorescence was completely quenched and replaced with a red-shifted emission that was assigned to the anthracene end-caps. This begs the question of why the fluorescence is quenched when an anthracene end-cap is used, whereas when a T₃ end-cap is used a mixed excited state is the result, even though the energy difference between PPE and anthracene is similar to that for PPE and T₃. The answer likely lies in the considerably different molecular orbital and excited state symmetries of the two end-groups. The symmetry of the T₃ end-group is the same as that of the polymer, allowing for good excited state mixing. However, the 9-anthracenyl end-group is polarized orthogonally to that of the polymer. The result of this is that mixing between the 9-anthracenyl end-group and the polymer chain is low, and thus the polymer chain is not well conjugated into the 9-anthracenyl end-group.

It is important for the hole transfer experiments described below that the end-group used is in a symmetry-allowed conjugation with the polymer chain, as the ultimate objective of this study is to measure the rate of charge transport through a conjugated system. If the end-group orbitals did not mix well with those of the polymer main chain,
then the rate limiting step in charge transport would be “hopping” across the non-conjugated bridge to the end-cap, and it would be impossible in principle to measure the rate of transport through the conjugated portion of the polymer. Thus, the 9-anthracenyl end-capped polymers would have been a poor choice for this study.

To confirm the idea that energy *interchain* energy transport is significantly different than *intrachain* transport, the fluorescence of the polymers were also measured in the solid state. The results are shown in Figure 2-7. When comparing the fluorescence of the PPE_{164} as a film to the solution-state fluorescence, it is clear that the emission from the film is broader with a loss of structure and red-shifted when compared to the emission in dilute solution. These effects are associated with inter-chain aggregation in the solid.

![Figure 2-7. Thin film fluorescence of PPE_{164}(---) and T_{3}PPE_{13} (——)](image-url)
The change in emission properties of T₃PPE₁₃ when going from solution to the solid is quite dramatic. Whereas the solution emission shows a significant amount of “PPE-like” fluorescence, this main emission band is completely quenched in the solid state and replaced by a broad band with little structure and $\lambda_{\text{max}} = 523$ nm. The reason for this difference lies in the different mode of exciton transport in the solid state as compared to in solution. In a film, the primary mode of transport in the film is *inter* chain exciton hopping. The distance between an end-cap “trap” and any exciton is much less in the solid than in solution because excitations may migrate between chains instead of just “walking down” one of them. Thus, exciton migration in films is expected to be more efficient than in solution, and this is borne out by experimental evidence.

**Biphenylene based polymers**

The biphenylene based polymers showed essentially identical photophysical properties as their phenylene based analogues. The absorption and emission spectra of these polymers is shown in Figure 2-8. The primary feature of in the absorption of both BpE₂₁ and T₃BpE₁₂ is a long-axis polarized $\pi \rightarrow \pi^*$ band, which in both cases is blue-shifted somewhat with respect to the phenylene based polymer. The end-capped polymer also exhibits a tail at the low-energy end of the spectrum, which is explained by conjugation with the low-energy T₃ end-group, by analogy to the all phenylene polymer.

The emission spectra of both copolymers are dominated by the zero-phonon transition. The main difference between the phenylene and biphenylene based polymers is in the “green” end-cap based component of the emission. This additional band, with a maximum at 490 nm, is due to emission from the low energy end-cap. As in the phenylene based polymer, the end-cap emission the result of orbital mixing between the thiophene-based end-groups and adjacent phenylene units. The end-cap’s contribution to
the overall emission spectrum is noticeably weaker in T$_3$BpE$_{12}$ than in T$_3$PPE$_{13}$. This indicates that energy transport in biphenylene based PPE’s is somewhat less efficient than in the phenylene based PPE’s, an effect that may be related to the fact that the biphenylene-based polymers can more readily adopt a non-planar “twisted” conformation than the all-phenylene based polymers.

![Graph showing absorption and emission](image)

**Figure 2-8.** Absorption and emission of BpE$_{21}$ (---) and T$_3$BpE$_{12}$ (——)

**Radiolytic production of cation and anion radicals**

Radical cations and radical anions were produced on PAE’s in solution by pulse radiolysis. These experiments were conducted at the Laser Electron Accelerator Facility (LEAF) at Brookhaven National Laboratories. This facility has been described previously in detail,$^{91,92}$ so only a brief description will be provided here. Figure 2-9 is a
schematic representation of the LEAF. LEAF is essentially a pulse-radiolysis facility. However, unlike traditional radiolysis instrumentation, which can only produce electrons beams with long pulse width, LEAF is able to produce high energy electrons with pulse widths as small as 5 ps. This is accomplished by using a photocathode as the electron source, and exciting it with a fast pulsed laser. The short pulse width of the laser translates into a short pulse width of electrons.

Figure 2-9. Schematic representation of the LEAF facility.

The generation of PAE-based ion radicals involves a series of reactions in which high energy electron pulses are converted into strongly oxidizing solvent cation radicals or holes (h⁺) or electrons (e⁻), which are then transferred to PAE chains.

At the LEAF, the electrons involved in radiolysis have an energy of 10 MeV and a pulse width <120 ps. The high energy electrons pass completely through the solution and exit the spectrophotometric cell, however, each electron produces roughly $10^4$ ionizations
that result in thermalized solvated electrons and solvent radical cations in concentrations of a few µM.

The precise nature of the reactions depends strongly on the solvent. 1,2 dichloroethane (DCE) for example, captures the electrons immediately to form radicals and Cl− ions.93,94 In tetrahydrofuran (THF) the solvent cation radicals decompose to radicals and solvated protons. Thus the net effect of the electron pulses is the production of thermalized solvent cation radicals (h+) in DCE and thermalized solvated electrons (e−) in THF. Because holes in DCE and electrons in THF attach to the desired analyte only after diffusion, formation of the desired radical cation or anion species is a bimolecular process. Since the analyte is always present in excess in these experiments, these reactions are pseudo-first order, and the observed rates of h+ or e− transfer to analyte depends upon analyte concentration and the bimolecular rate constant for reaction of h+ or e− with the analyte. A fraction of h+ in DCE and e− in THF are lost by reactions with counter ions, however, these reactions are measured and taken into account in the results.

**Electron and hole transport to polymers following radiolysis**

A series of experiments were carried out in order to determine the bimolecular rate constants for h+ and e− trapping reactions, i.e. k2-2 and k2-3,

\[
\begin{align*}
\text{PAE} + (\text{PhMe})_2^{•+} & \rightarrow \text{PAE}^{•+} + 2 \text{PhMe} \\
\text{PAE} + e_{s}^{-} & \rightarrow \text{PAE}^{•−} + 2 \text{PhMe}
\end{align*}
\]

Reactions 2-2 and 2-3 are both strongly exoergic (ΔG0 < -0.5 eV), and occur with diffusion controlled rates. It is important to note that the “rate constants” reported in this discussion are not in fact constant, although they do not vary significantly within the time
of the reactions under study. The experimentally observed pseudo-first order decays are 
therefore nearly exponential. Consequently, the rate constants reported herein are 
effective or “average” rate constants which represent best fits to the observed pseudo-first 
order kinetic traces for the rise of the absorption due to the creation or PAE radical ions. 
If the range of concentrations of polymer was significantly higher or lower, these 
constants would have somewhat different values.

The species produced by radiolysis of PPE$_{164}$ in DCE/toluene reacts with TMPD, a 
good hole scavenger, with a bimolecular rate $k = 2.8 \times 10^9$ M$^{-1}$ s$^{-1}$ to produce TMPD$^\cdot$. 
This is confirmed by the observation of the characteristic absorbances of TMPD$^\cdot$ at 570 
nm and 620 – 630 nm.$^{95}$ Also, the species produced as a result of radiolysis of PPE$_{164}$ in 
THF reacts with tetracyanoethylene (TCNE) and chloranil to give species with the 
characteristic absorbance bands of TCNE$^\cdot$ and chloranil$^\cdot$. $^{95}$ On this basis, the product of 
PAE radiolysis in DCE/toluene can be assigned as the radical cation and the product of 
PAE radiolysis in THF can be assigned as the radical anion.

The effective rate constants for the bimolecular reactions of h$^+$ (in DCE/toluene) 
and e$^-$ (in THF) formed by pulse radiolysis with PAE’s to produce radical cations and 
anions (respectively) of the polymers is presented in Table 2-3. The bimolecular rate 
constants are reported with respect to both polymer and repeat unit concentration. There 
are several points worth noting with respect to this data. First, the experimentally 
determined rate constants for growth of the PAE radical ions, as expressed per monomer 
repeat unit, is significantly lower than the expected diffusion controlled reaction between 
two small molecules. Second, in general the rates for electron transfer to PAE are
considerably greater than the rates for hole transfer. This difference is due to the faster
diffusion rate of $e^-$.96-99

Table 2-3. Reaction rate constants of poly-(arylene ethynylene)s (PAEs) and
terthiophene end-capped PAEs with positive and negative charge carriers in
solution.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>$N$</th>
<th>$k$ (M$^{-1}$ s$^{-1}$)</th>
<th>$k_{(monomer)}$ (M$^{-1}$ s$^{-1}$)$^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>PPE$_{164}^+$ (MeΦ)$_2^{**}$</td>
<td>164</td>
<td>2.1 x 10$^{11}$</td>
<td>1.3 x 10$^9$</td>
</tr>
<tr>
<td>PPE$_{24}^+$ (MeΦ)$_2^{**}$</td>
<td>24</td>
<td>4.8 x 10$^{10}$</td>
<td>2.0 x 10$^9$</td>
</tr>
<tr>
<td>PBpE$_{21}^+$ (MeΦ)$_2^{**}$</td>
<td>21</td>
<td>5.1 x 10$^{10}$</td>
<td>2.4 x 10$^9$</td>
</tr>
<tr>
<td>T$<em>3$PPE$</em>{13}^+$ (MeΦ)$_2^{**}$</td>
<td>13</td>
<td>7.1 x 10$^{10}$</td>
<td>5.5 x 10$^9$</td>
</tr>
<tr>
<td>T$<em>3$PbpE$</em>{12}^+$ (MeΦ)$_2^{**}$</td>
<td>12</td>
<td>3.0 x 10$^{10}$</td>
<td>2.4 x 10$^9$</td>
</tr>
<tr>
<td>T$_2^+$ (MeΦ)$_2^{**}$</td>
<td>1.1 x 10$^{10}$</td>
<td>5.3 x 10$^9$</td>
<td></td>
</tr>
<tr>
<td>T$_3^+$ (MeΦ)$_2^{**}$</td>
<td>1.7 x 10$^{10}$</td>
<td>5.5 x 10$^9$</td>
<td></td>
</tr>
<tr>
<td>T$_3$ + [MeΦ:Cl$^+$]</td>
<td>5.0 x 10$^9$</td>
<td>1.7 x 10$^9$</td>
<td></td>
</tr>
<tr>
<td>T$_4^+$ (MeΦ)$_2^{**}$</td>
<td>-$^b$</td>
<td>-$^b$</td>
<td></td>
</tr>
<tr>
<td>T$_4$ + [MeΦ:Cl$^+$]</td>
<td>4.1 x 10$^9$</td>
<td>1.0 x 10$^9$</td>
<td></td>
</tr>
<tr>
<td>PPE$<em>{164}^+$ e$^-</em>{THF}$</td>
<td>164</td>
<td>4.7 x 10$^{12}$</td>
<td>2.8 x 10$^{10}$</td>
</tr>
<tr>
<td>PBpE$<em>{21}^+$ e$^-</em>{THF}$</td>
<td>21</td>
<td>1.3 x 10$^{12}$</td>
<td>6.3 x 10$^{10}$</td>
</tr>
<tr>
<td>T$<em>3$PPE$</em>{13}^+$ e$^-_{THF}$</td>
<td>13</td>
<td>7.1 x 10$^{11}$</td>
<td>5.5 x 10$^{10}$</td>
</tr>
<tr>
<td>T$<em>3$PbpE$</em>{12}^+$ e$^-_{THF}$</td>
<td>12</td>
<td>3.5 x 10$^{11}$</td>
<td>2.8 x 10$^{10}$</td>
</tr>
</tbody>
</table>

$^a$ For comparison to small molecules the average rate constant per repeat unit is reported. For T$_3$-containing
polymers the T$_3$ was not included.

$^b$ Could not be measured due to absorption of the product cation at 1000 nm.

Poly(arylene ethynylene)s are known to aggregate in solution. The degree of
aggregation is dependant on both the solvent system and the concentration of the
polymer.$^{22,50}$ The pseudo-first order growth of PPE$_{164}^{**}$ as a function of polymer
concentration is linear when the concentration is less than 1.35 x 10$^{-3}$ M in repeat units.

This suggests that aggregation is not an important factor in DCE/toluene solution at the
concentration ranges used in these studies. Since THF is a better solvent for PAE’s than DCE/toluene, it is unlikely that aggregation is a factor in that medium either.

**Semi-empirical calculations: spectroscopy of PPE-based ion radicals**

Before examining the spectra of PAE ion radicals, it is useful to use theory to attempt to provide insight into the expected electronic transitions. Thus, semi-empirical calculations (ZINDO/S, CI = 6,6, AM1u geometries) on a series of PPE-type model oligomers, \([\text{Ph-(-C≡C-Ph-)}_n\text{-H}]^{+}\) (structure in Figure 2-10), were carried out.\(^{100}\) The Zindo/S calculations predict two optical transitions with energies that decrease with increasing oligomer length, \(n\). With the exception of the shortest member of the series (i.e., diphenylacetylene, \(n = 1\)) the lowest energy transitions in the radical cations derive primarily from a strongly allowed, one-electron transition from the HOMO-1 to the half-occupied HOMO (SOMO) as indicated schematically in Figure 2-9. (Here HOMO and LUMO refer to the orbitals that are the highest occupied and lowest unoccupied in the neutral parent molecule.) This low-energy transition is predicted to occur in the near IR region, and its energy is expected to vary strongly with the length of the PPE segment. The calculations predict that a second, higher energy transition will occur in the visible region. This transition is primarily of HOMO (SOMO) \(\rightarrow\) LUMO character.

Furthermore, the calculations predict that the energy of this transition varies only weakly with oligomer length. Similar results are obtained for the anion radicals, however, in this case the near IR bands derive primarily from the LUMO (SOMO) \(\rightarrow\) LUMO + 1 transition (see Figure 2-10).
Figure 2-10. Transition energies computed for radical cations of phenylene ethynylene oligomers as a function of length, n. The energy of the lowest allowed transition (o) is very sensitive to length, while the energy of the strong transition in the visible (+) changes little with n. The simple MO diagram at right indicates the nature of the transitions, determined from the CI calculation. Calculations were ZINDO/S for at AM1u geometries of the cations.

Visible/Near-IR Spectroscopy of Charged PAEs

Radical anions

By monitoring the wavelength dependence of the transient absorption of PAE solutions at a fixed delay time following the e⁻ pulse it is possible to construct the visible-near IR absorption spectra of the PAE-based radical ions. The delay time used is dependent upon the concentration of polymer and the bimolecular rate constant for charge transfer from the solvent to the polymer. Generally in these experiments the delay times used were of the order of 0.1-1.0 µs. The time was chosen to follow the growth of the radical ion species under observation and precede its decay. It is possible to estimate
the molar absorptivity ($\varepsilon$, M$^{-1}$cm$^{-1}$) of the PAE radical ions based on radiolysis yields of (PhMe)$_2$•$^+$ in DCE/toluene and $\varepsilon_8^-$ in THF. The resulting spectra for a variety of PAE-based radical ions, along with the spectra of the T$_3$ oligomer based radical ions, are illustrated in Figure 2-11.

Figure 2-11. Spectra of cations and anions of poly(phenylene ethynylenes) (♦), endcapped poly(phenylene ethynylenes) (▲) and T$_3$ (●) where a) is the spectrum of PBpE$_{21}$•-, T$_3$PBpE$_{12}$•- and T$_3$•- in THF, b) is the spectrum of PPE$_{164}$•-, T$_3$PPE$_{13}$•- and T$_3$•- in THF, c) is the spectrum of PBpE$_{21}$•+ and T$_3$PBpE$_{12}$•+ in DCE/toluene and T$_3$•+ in DCE and d) is the spectrum of PPE$_{164}$•+ and T$_3$PPE$_{13}$•+ in DCE/toluene and T$_3$•+ in DCE. The polymer concentrations were in the range 0.6 - 2.8 mM in repeat units and delay times were in the range 0.1 – 1.0 µs.
Figure 2-11a shows the spectra of the radical anions of $T_3^-$ and the biphenyl-based PAEs, $\text{PBpE}_{21}^-$ and $T_3\text{PBpE}_{12}^-$. All of these anion radicals feature two absorption bands: one relatively sharp band in the visible region and a second broader band in the near-IR. These two bands are intense, with molar absorptivities ($\varepsilon$) greater than 50,000 M$^{-1}$cm$^{-1}$. The observed spectra are qualitatively consistent with the predictions of Zindo/S calculations, which supports their assignment to PBpE-based radicals. The experimentally observed absorption bands occur at $\lambda_{\text{max}} \approx 600$ and 1100 nm in $T_3^-$, while in $\text{PBpE}_{21}^-$ and $T_3\text{PBpE}_{21}^-$ $\lambda_{\text{max}} \approx 625$ and $> 1600$ nm. It is noteworthy that the lower energy band of PBpE anion radical is considerably broader and red-shifted than the band for the $T_3$ anion radicals. This indicates that the electron is considerably more delocalized in the former.

Even more significantly, the spectra of $\text{PBpE}_{21}^-$ and $T_3\text{PBpE}_{21}^-$ are essentially identical, indicating that $T_3$ end-caps do not influence the spectrum of $T_3\text{PBpE}_{21}^-$. Thus, the electron is not localized on the $T_3$ end-groups in the end-capped polymer; it is instead delocalized on the PBpE main chain. This is constant with expectation because $T_3$ is more electron rich than PBpE, and its LUMO is therefore likely to be higher in energy than that of PBpE.

Figure 2-11b shows the spectra of the radical anions of the phenylene based polymers. Like in the biphenylene-based polymers, the $T_3$ end-cap has no effect on the spectra, which exhibit $\lambda_{\text{max}} \approx 625$ and $> 1600$ nm for both $\text{PPE}_{164}^-$ and $T_3\text{PPE}_{13}^-$. This result is expected, and indicates that there radical anion is again located on the polymer main chain and not on the end-caps.
Radical cations

Figure 2-11 also depicts the absorption spectra of the T₃PBpE₁₂⁺⁺, PBpE₂₁⁺⁺, and T₃⁺⁺ radical cations. All of the spectra feature two strong absorption bands, one in the visible and a second in the near-IR, consistent with the Zindo/S predictions. The bands in T₃⁺⁺ are observed at \( \lambda_{\text{max}} \approx 550 \) and 850 nm, in good agreement with the previously reported spectrum of this species. The two bands appear at \( \lambda_{\text{max}} \approx 600 \) and 1150 nm in PBpE₂₁⁺⁺ and T₃PBpE₁₂⁺⁺. With respect to the biphenylene based polymers, the most significant feature of these two spectra is that they are essentially identical. This strongly suggests that in T₃PBpE₁₂⁺⁺ the hole resides on the PBpE chain and is not trapped by or localized on the T₃ end-caps. This result, while initially surprising, is confirmed on the basis of oxidation potentials estimated by bimolecular hole transfer equilibrium experiments (see below). From this data, it is evident that the \( E_{\text{ox}} \) of T₃ is somewhat greater than that of PBpE. Thus at equilibrium PBpE⁺⁺ is favored over T₃⁺⁺ (i.e. the equilibrium in equation 2-4 lies to the left).

\[
\text{T₃-(PBpE}^{\text{**}}\text{-T₃) \leftrightarrow T₃-(PBpE)-T₃}^{\text{**}} \quad \text{(2-4)}
\]

Figure 2-11d compares the spectra of PPE₁₆₄⁺⁺ and T₃PPE₁₃⁺⁺. The spectra of these species are noticeably different. While PPE₁₆₄⁺⁺ features two bands at \( \lambda_{\text{max}} \approx 600 \) and 1950 nm, the visible band is red-shifted to \( \lambda_{\text{max}} \approx 640 \) nm and the near-IR band is blue shifted to \( \lambda_{\text{max}} \approx 1350 \) nm in T₃PPE₁₃⁺⁺. The spectrum of PPE₂₄⁺⁺ (not shown), was the same as that of PPE₁₆₄⁺⁺. This result indicates that the differences in the spectra of PPE₁₆₄⁺⁺ and T₃PPE₁₃⁺⁺ are not simply due to the differences in the degrees of polymerization of the two polymers. The differences in the spectra strongly imply that
the hole in the end-capped polymer is trapped on the T₃ end group. However, although the presence of the end group does have an effect on the spectrum of the cation radical, the spectrum of the hole on the end-capped polymer is distinctly different from that of the end group cation radical, T₃⁺⁺. Specifically, the low energy transition in T₃PPE₁₃⁺⁺ is red shifted and broader compared to the analogous transition in T₃⁺⁺.

Some insight into this observation can be garnered from the spectrum of the cation radical of the end-group model, Ph- T₃⁺⁺, which is shown in Figure 2-12. This spectrum features narrow bands at max ≈ 620 and 1050 nm. That these bands are at wavelengths intermediate between the observed bands in T₃⁺⁺ and T₃PPE₁₃⁺⁺ suggests that the cation radical is delocalized onto the phenylene adjacent to the terthienyl end-cap.

![Figure 2-12](image)

**Figure 2-12.** Differential absorbance spectra of Ph- T₃⁺⁺ (solid line) and T₃⁺⁺ (dashed line). The spectra were obtained by photo induced electron transfer to methyl viologen, and recorded 400 ns after the laser pulse. Note that this T₃⁺⁺ spectra is identical to the radiolytically generated spectra.
This idea is further supported by calculations. AM1 level molecular orbital calculations indicate that while the species’ HOMO resides predominantly on the T3, there is a significant orbital density on several adjacent phenylene units. Figure 2-13 shows this graphically. These results indicate that the cation radical T3PPE$_{13}$•$^+$ is not localized on the end-cap. Instead, it is somewhat *delocalized* into the polymer main chain.

This provides an explanation as to why the absorption spectrum of T3PPE$_{13}$•$^+$ is not a simple linear combination of spectra for T3•$^+$ and PPE$_{164}$•$^+$. Additionally, the low energy band in T3PPE$_{13}$•$^+$ is considerably red-shifted and much broader than in T3•$^+$. These facts support the notion that the hole in the end-capped polymers is delocalized significantly more than in the terthiophene end-cap alone. It is noteworthy that there is likely to be an equilibrium established involving hole-transfer from the end-group to the main chain, as in equation 2-5. This equilibrium may also have an effect on the observed spectrum.

\[
\text{T}_3-(\text{PPE}^{•+})-\text{PPE}^{•+} \rightleftharpoons \text{PPE}^{•+}-(\text{T}_3^{•+})^{•+}
\]
Bimolecular Hole Transfer Reactions: Thermodynamics of Intrachain PPE $\rightarrow$ T$_3$

Hole Transfer

In order to explain the surprising result that holes are not trapped by the T$_3$ end-groups in T$_3$PBPbE$_{12}^{*+}$, experiments involving bimolecular hole transfer from a variety of 2,5-oligothienyls (T$_n$, n = 1, 2, 3, 4) were performed. These experiments were designed to determine the energetics of intra-chain hole transfer by measuring the position of the equilibria, and the rate constants, for the following series of hole-transfer reactions.

\[
\begin{align*}
\text{PAE}^{*+} + \text{T}_2 & \quad \leftrightarrow \quad \text{PAE} + \text{T}_2^{*+} \\
\text{PAE}^{*+} + \text{T}_3 & \quad \leftrightarrow \quad \text{PAE} + \text{T}_3^{*+} \\
\text{PAE}^{*+} + \text{T}_4 & \quad \leftrightarrow \quad \text{PAE} + \text{T}_4^{*+}
\end{align*}
\]

(2-6)  
(2-7)  
(2-8)

Using the reported oxidation potentials for the T$_n^{0*+}$ couples,\textsuperscript{102} and the experimentally determined equilibrium constants for each of the above reactions, the redox potentials ($E^{\circ}_{\text{ox}}$) for the polymers were determined. Cyclic voltammetry, (CV) both in the solid state and in solution, was attempted to confirm these results, however, CV experiments proved unsuccessful, giving only broad, irreversible waves at 1.1 – 1.3 eV.

Table 2-4 is a compilation of experimentally determined rate and equilibrium constant data, and Figure 2-14 provides a redox scale summarizing the $E^{\circ}_{\text{ox}}$ values. An example of the data used in these measurements is provided in Figure 2-15. These measurements unambiguously show that the oxidation potentials for all of the polymers are bracketed between the potentials for T$_2$ and T$_4$ (1.25 V > $E^{\circ}_{\text{ox}}$ > 0.80 V), while equilibria are established with T$_3$. 
Table 2-3. Bimolecular rate and thermodynamic data for reactions of PAE’s with thiophene oligomers.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>n</th>
<th>$K$ ($M^{-1} s^{-1}$)</th>
<th>$K_{eq}$</th>
<th>$\Delta G^\circ (mV)^a$</th>
<th>$E_{ox}$ (V) vs. SCE</th>
</tr>
</thead>
<tbody>
<tr>
<td>PPE$_{164}^{••}$ + T$_2$</td>
<td>164</td>
<td>$-(2.5 \pm 1.5) \times 10^{11}$</td>
<td>$(1.0 \pm 0.5) \times 10^{-3}$</td>
<td>177 ± 40</td>
<td>1.03 ± 0.04</td>
</tr>
<tr>
<td>PPE$_{164}^{••}$ + T$_3$</td>
<td>164</td>
<td>$4.5 \times 10^9$</td>
<td>0.82</td>
<td>5.2</td>
<td>0.91 $^a$</td>
</tr>
<tr>
<td>PPE$_{24}^{••}$ + T$_3$</td>
<td>24</td>
<td>$3.6 \times 10^9$</td>
<td>6.0 ± 2</td>
<td>-46</td>
<td>0.96 $^a$</td>
</tr>
<tr>
<td>PPE$_{164}^{••}$ + T$_4$</td>
<td>164</td>
<td>$5.6 \times 10^9$</td>
<td>&gt; 1.7</td>
<td>&lt; -14</td>
<td></td>
</tr>
<tr>
<td>PBpE$_{21}^{••}$ + T$_2$</td>
<td>21</td>
<td>-</td>
<td>$&lt; 4.1 \times 10^{-2}$</td>
<td>&gt; 82</td>
<td>&lt; 1.13</td>
</tr>
<tr>
<td>PBpE$_{21}^{••}$ + T$_3$</td>
<td>21</td>
<td>-</td>
<td>0.12</td>
<td>55</td>
<td>0.86 $^a$</td>
</tr>
<tr>
<td>PBpE$_{21}^{••}$ + T$_4$</td>
<td>21</td>
<td>$4.4 \times 10^9$</td>
<td>&gt; 6.3</td>
<td>&lt; -47</td>
<td>&gt; 0.81 $^a$</td>
</tr>
<tr>
<td>T$<em>3$PPE$</em>{13}^{••}$ + T$_3$</td>
<td>13</td>
<td>-</td>
<td>1.1</td>
<td>-1.3</td>
<td>0.91 $^a$</td>
</tr>
<tr>
<td>T$<em>3$PPE$</em>{13}^{••}$ + T$_4$</td>
<td>13</td>
<td>$3.8 \times 10^9$</td>
<td>&gt; 45</td>
<td>&lt; -98</td>
<td>&gt; 0.86 $^a$</td>
</tr>
</tbody>
</table>

$^a$ Estimated uncertainties in $-\Delta G^\circ$ or $E_{ox}$ are (+10, -40 mV) for reactions with T$_3$ and T$_4$ due to uncertain contributions from a second oxidizing species and to formation of an unknown species at longer times (see text).

$^b$ Oxidation potentials for the polymers based on reported potentials $E_{ox}^\circ$ = 1.25 (T$_2$), 0.95 (T$_3$) and 0.80 (T$_4$) in V vs. Ag/AgCl$^{103}$ were converted to SCE reference by subtracting 44 mV to give 1.21, 0.91 and 0.76. See note $^a$.

$^c$ The sign indicates that this is the reverse reaction. Only the reverse reaction (a transfer of charge from T$_2^{••}$ to PPE) was observed.

The experimentally determined equilibrium constants provide an explanation for the fact that the T$_3$ end-caps capture holes in the case of the phenylene polymer, but not in the biphenylene polymer. $E_{ox}^\circ$ for the biphenylene polymer is approximately 100 mV lower than in the phenylene analogue. This difference is significant enough that the equilibrium constant for the hole-transfer reaction between PBpE$_{21}$ and T$_3$ strongly favors placing the hole on the polymer whereas in the case of the phenylene the equilibrium favors the hole residing on the end-cap. Another significant result of these experiments is that hole injection into PPE$_{164}$ is thermodynamically favored over injection into PPE$_{24}$ by a factor of $8 \pm 2.5$. This is nearly identical to the ratio of their chain lengths (6.8), and
very likely reflects entropic factors which favor the hole on the longer chain. If \( L \) is the delocalization length of a charge carrier, in repeat units, then there are \( D_p - L \) ways to place a charge in a polymer with a given degree of polymerization. Thus the ratio of the equilibrium constants for two polymers whose degrees of polymerization are \( D_{p1} \) and \( D_{p2} \) should be \( K(D_{p1})/K(D_{p2}) = (D_{p1} - L)/(D_{p2} - L) \). As a consequence, these results imply that the delocalization length of a hole, \( L \), is slightly less than 10 repeat units, or twenty phenylene rings. Furthermore, \( K_{eq} \) for the reaction between \( \text{T}_3\text{PPE}_{13}^+ \) and \( \text{T}_3 \) is about 1, leading to the surprising conclusion that the charge on the end-capped polymer is not stabilized due to the delocalization of the end groups. This likely reflects a balance between the destabilizing electron withdrawing effects of the PAE main-chain\(^{104}\) and the stabilization associated with delocalization of the \( \text{T}_3 \) HOMO into the polymer chain.

![Figure 2-14](image.png)

Figure 2-14. Schematic of the oxidation potentials of various PAE’s and thiophene oligomers. The potentials are vs. SCE.
Figure 2-15. Absorbance (1000 nm) as a function of time after an electron pulse for solutions of PPE$_{164}$ (PPE) and varied concentrations of terthiophene (T3) in 1,2-dichloroethane + 1.6 M toluene. At this wavelength, the absorbance is due almost entirely to the polymer cation radical. The rate of charge transfer and the equilibrium are evident from this data, along with the complication that an additional species is formed at long times, especially at the highest concentration of T3, 216 µM. At short times, (<0.5 µs) the strong absorption of the dimeric toluene cation radical (MePh$_2$•+) is evident, most noticeably in the trace of the experiment with only 0.39 mM T$_3$.

The use of electron transfer equilibria to obtain oxidation potentials typically involves errors of only a few mV. However, the uncertainties in the equilibrium constants and free energy changes reported here are reduced due to complexities inherent in the system. The Cl•-toluene π-charge transfer complex (Cl:PhMe) oxidizes PAE’s only slowly if at all, but it does oxidize T$_3$ and T$_4$ to their radical cations. This fact, and the limited lifetime of Cl:PhMe means that the number of ions entering into equilibria change with the concentration of T$_3$ and T$_4$. Another complexity arises relating to the slow formation of an unknown species, possible a hetero-dimer between T$_3$ and PAE••.
that causes limitations in the ability to work at higher reactant concentrations. These effects contribute to the uncertainties reported for the free energy changes in Table 2-3.

**Dynamics of Interchain Hole Transfer**

As noted in the introduction to this chapter, one goal of this work is to determine the dynamics of intrachain hole transfer through the conjugated PPE. When holes are injected into T₃PPE₁₃ more than 80% are likely to be captured by the long PPE segment, which consists of an average of 26 phenylene rings. This preference arises because of the high exothermicity of hole transfer from the primary donor, (PhMe)₂⁺, and the fact that there is a much higher concentration of phenylene moieties than thiophene end-caps. However, at the earliest times accessible after radiolysis, the only observable product in T₃PPE₁₃ is a species where the hole already resides on the end-cap. This means that intramolecular hole transfer is faster than the bimolecular hole capture reaction between the solvent and the polymer. With a saturated solution of T₃PPE₁₃ ([PRU] = 1.6 mM), the rate constant for hole attachment is $3.6 \times 10^{10} \text{ M}^{-1}\text{s}^{-1}$. Thus, while an accurate figure for $k_{HT}$ cannot be reported at the present time, it is possible to ascertain a lower limit of $1 \times 10^8 \text{ s}^{-1}$.

**Conclusions**

In summary, PPE molecular wires with two different architectures one based on phenylene and the other on biphenylene, were synthesized both in their pristine form and with terthiophene end-caps. The ultraviolet and visible absorption and photoluminescence spectroscopy of these materials indicate that their excited state is not completely localized on the oligo thiophene endgroup, but is instead somewhat delocalized into the polymer main chain. This idea was confirmed by studying model compounds and by Zindo/S calculations.
The cation and anion radicals of the polymers were generated by pulse radiolysis at the LEAF at Brookhaven National Laboratories. Both radicals show transitions in the visible and IR that agree with the reported theoretical predictions for species of this type. The anion radicals of the end-capped species are not trapped by terthiophene, which is the expected result considering that terthiophene is more electron rich than the polymer backbone. The cation radicals of the phenylene based polymer are trapped by the end-cap, although as in the case of the exciton, the charge is somewhat delocalized into the polymer main chain. On the other hand, in the case of the biphenylene based polymer, cation radicals are not trapped by the end groups and remain on the polymer main chain. This result is explained by bimolecular hole transfer experiments which show that the oxidation potential of the biphenylene based polymer is somewhat higher than that of the end-group. These same bimolecular hole transfer experiments are used to determine the oxidation potentials of the parent and end-capped polymers.

It was hoped that this investigation would allow for the determination of the rate constant associated with the transfer of a radical cation from the main chain of a PPE to the terthiophene end cap. Unfortunately, this process is much faster than capture of holes by the polymer, indicating that the rate of hole transfer is greater than $1 \times 10^8 \text{ s}^{-1}$. This result is expected from the absorption spectra of the parent polymers, which indicate that the charges are highly delocalized in the polymer chain. It is likely that charge transport is much faster than the limit observed in these experiments, pointing to the desirability of developing new and more effective methodologies for charge injection on ultrafast timescales.
Experimental Section

Materials and General Synthesis

1,2-Dichloroethane (Aldrich) was HPLC grade and dried over type 4 Å molecular sieves prior to use. Anhydrous 99.8% toluene (Aldrich) was used as received. Tetrahydrofuran (Aldrich, anhydrous) was distilled from LiAlH₄ and then from sodium/benzophenone and stored in an environment of argon. 2,2’-Bithiophene, 2,2’:5’,2’’-terthiophene (T₃), 2,2’:5’,2’’’:5’’,2’’’-quaterthiophene (T₄), tetramethylphenylenediamine (TMPD), tetracyanoethylene (TCNE), 2,3,5,6-tetrachlorobenzoquinone (chloranil), 1,4-iodobenzene, 1,4-dimethoxybenzene, Pd(PPh₃)₄ and CuI were purchased from Aldrich or Acros. Quaterthiophene was recrystallized from toluene and 2,2’-bithiophene, TMPD, TCNE and chloranil were sublimed prior to use and the other compounds were used as received. 2-Iodo-5:2’,5’:2’’-terthiophene (I-T₃) was prepared by a literature procedure. Chromatography was carried out using silica gel (Merk, 230-400 mesh). NMR spectra were obtained on Varian Gemini or VXR spectrophotometers operating at 300 MHZ or an Inova spectrophotometer operating at 500 MHZ.

Synthetic Procedures

2,5-Diiodo-1,4-dimethoxybenzene. This compound was prepared by a modified literature procedure. A solution of potassium periodate (8.0 g, 35 mmol) in water (30 mL) was added to a round bottom flask charged with 1,4-dimethoxybenzene (6.9 g, 50.0 mmol) and iodine (12.7 g, 50.0 mmol) and acetic acid (120 mL). The flask was fitted with a condenser, and the solution was heated to a gentle reflux with stirring. After attaining reflux, a solution of sulfuric acid (3.0 mL in 15 mL water) was added slowly through the condenser. An exothermic reaction was observed after addition of the first
few drops of acid solution, and the heating was suspended temporarily until addition of the sulfuric acid was complete. The reaction was then returned to reflux. After approximately 30 minutes, the brown iodine color of the solution appeared significantly lighter. (Caution: While the solution is refluxing, crystals of iodine sublime into the condenser, and it is necessary to use a long glass rod to push these crystals back into the solution. If the condenser becomes completely clogged with iodine, an explosion may result due to the buildup of gas pressure in the system.) When 1.5 hours had elapsed after the addition of sulfuric acid, heat was removed from the reaction and it was allowed to cool to room temperature. The solution was then treated with a saturated aqueous solution of Na₂S₂O₄ until no iodine color was noticeable. The reaction mixture was diluted with water to double the original volume to induce precipitation of the product as yellow crystals. The solid is collected by vacuum filtration, washed with water, and recrystallized from hot acetone/water giving the desired product as a white, crystalline solid, yield 17.4 g (89%).

**2,5-Diodo-1,4-dihydroquinone.** This compound was prepared by a modified literature procedure. A 500 mL Erlenmeyer flask with a ground-glass top was charged with 2,5-diiodo-1,4-dimethoxybenzene (30.0 g, 76.9 mmol) and 350 mL methylene chloride (previously dried over P₂O₅). The resulting solution was cooled in a bath of ethanol and liquid nitrogen, and fitted with a condenser. Neat BBr₃ (38.5 g, 14.5 mL, 153.8 mmol) was added slowly through the condenser. After the addition was complete, a septum cap was affixed to the top of the condenser, and a gentle flow of N₂ gas was introduced to the reaction through a needle. The mixture was allowed to warm to room temperature, then heated to reflux and stirred for 48 hours. After this time, small portions
of methanol and then water were added to the solution. Methylene chloride was evaporated by rotory evaporation and the residue was diluted with methanol-water (80:20). A few spatula tips of sodium sulfite (Na$_2$SO$_3$) was then added. The solution was then placed in the freezer overnight, after which fine off-white crystals of product formed and were collected by vacuum filtration, yield 24.9 g (89%).

**2,5-Bis-(2-ethylhexyloxy)-1,4-diiodobenzene.** This compound was prepared by a modification of a literature procedure.$^{105}$ To a solution of 2,5-diiodohydroquinone (4.24 g, 11 mmol) in methyl ethyl ketone (80 mL) in an Erlenmeyer flask with a ground-glass top was added potassium carbonate (15.2 g, 110 mmol). The system was fitted with a condenser, and a nitrogen inlet and outlet. The mixture was gently heated for 20 min with stirring to dissolve most of the potassium carbonate. Then 1-bromo-2-ethylhexane (2.5 mL, 44 mmol) was added via syringe. The system was then heated to reflux for 16 hours. Substantial amounts of salt precipitated over the course of the reaction. After reflux, 1 g of sodium sulfite (Na$_2$SO$_3$) was added to the mixture, and the solution was then neutralized by slow addition of 1 N aqueous HCl. The reaction mixture remained under positive nitrogen pressure, with an outlet to allow for the escape of gasses, during the entire process. After neutralization the mixture was further diluted with 100 mL of warm (40°C) water, and stirred for one hour. The mixture was then extracted with pentanes (3 x 40 mL) and the organic layer was dried over MgSO$_4$ and concentrated to a volume of 10 mL. The concentrated pentane solution was passed through a short (3” length, 2” diameter) column of silica by elution with 200 mL of pentanes, followed by evaporation of the solvent under reduced pressure afforded the desired product as a clear
liquid, yield 4.07 g, 63%. $^1$H NMR (CDCl$_3$): $\delta$ 0.9-1.8 (complex multiplet, 26H), 3.8 (t, 4H), 7.1 (s, 2H).

**1,4-Diethynylbenzene.** This compound was prepared by a modified literature procedure.$^{105}$ 1,4-diiodobenzene (18.0 g, 54.6 mmol), Pd(PPh$_3)_2$Cl$_2$ (0.4 g, 0.57 mmol) and CuI (0.1 g, 0.525 mmol) were dissolved in a mixture of THF and diisopropylamine (200 mL, 8:2) which has been previously deoxygenated by 30 min of bubbling with N$_2$. This solution was cooled with an ice bath whereupon trimethylsilylacetylene (20 mL, 13.9 g, 0.142 mmol) was added dropwise with stirring and under positive pressure of nitrogen. After a small volume (< 5 mL) was added, an endothermic reaction was observed with formation of a thick precipitate of white powder. After the addition was complete, the reaction was allowed to warm to room temperature and it was stirred an additional twenty-four hours. After this time, the reaction mixture was a dark color. The solvents were removed by rotory evaporation and the remaining black solid was washed several times with water and a water-methanol (40:60) mixture. The solid was then dissolved in hot hexane, decolorized with active charcoal, and passed through a short column of alumina. The resulting white solid was recrystallized from acetone/water to afford 1,4-bis-(trimethylsilylethynyl)benzene as shiny white crystalline flakes. The 1,4-bis-(trimethylsilylethynyl)benzene crystals were dissolved in a mixture of THF and methanol (80:20). To the resulting solution was added a solution of KF (10.0 g) and a spatula-tip of tetrabutylammonium bromide in water (80 mL). The resulting suspension was vigorously stirred at room temperature under N$_2$ for 12 hours, and then diluted with water until the product precipitated as a fine white powder. The solid was collected by
vacuum filtration, washed with water and recrystallized from methanol/water to afford 1,4-diethynylbenzene as a white solid, yield 5.6 g (81%).

4,4'-Diethynylbiphenyl. This compound was prepared by the same procedure as described above for 1,4-diethynylbenzene, except that 4,4'-diiodobiphenyl was used in place of 1,4-diethynylbenzene. The product was obtained as a white solid, yield for the two steps 75%.

1,4-Diundecyloxy benzene. A mixture of potassium carbonate (22 g, 0.16 mol) in methyl ethyl ketone (40 mL) in an erlenmeyer flask with a ground glass top was heated gently and stirred to dissolve most of the potassium carbonate. The solution was then sparged with argon for 15 minutes, after which time hydroquinone (5 g, 0.045 mol) and 1-bromo undecane (26 g, 0.10 mol) was added. The reaction mixture was fitted with a condenser and heated to reflux for 12 hours. A large volume of salt precipitated during the course of the reaction. After this time, the solution was cooled to room temperature and neutralized by slow addition of 1 N HCl. The reaction mixture was kept under a positive pressure of argon, with a vent to allow for escape of gasses, during this entire process. A few spatula tips of sodium sulfite were then added to the reaction mixture. The crude product was precipitated by pouring into a large quantity of ice-cold water, and the recovered by filtration as a tan solid. A portion of the product used for analysis was purified by recrystalization from methanol-water, but the crude material was used in the next step. The crude yield was 14.8 g (78%). 1H NMR (CDCl₃): δ 0.08 (t, 6 H), 1.6 (br, 32 H), 1.8 (m, 4 H), 3.9 (t, 4 H), 7.0 (s, 4 H).

2,5-Diundecyloxy-1,4-diiodo benzene. This product was obtained by the same procedure used to prepare 2,5-dimethoxy-1,4-diiodo benzene, except the amounts of
reagents used were: 1,4-diundecyloxy benzene (10 g, 0.024 mol), iodine (6.1 g, 0.024 mol) and potassium periodate (3.6 g, 0.016 mol). The product was purified by elution through a short plug of silica with hexanes, treatment with activated carbon and recrystallization from methanol-water. $^1$H NMR (CDCl$_3$): $\delta$ 0.08 (t, 6 H), 1.6 (br, 32 H), 1.8 (m, 4 H), 3.9 (t, 4 H), 7.0 (s, 4 H).

**Photophysical Methods**

UV-visible absorption spectra were obtained on a Varian Cary 100 spectrophotometer. Corrected steady-state emission spectra were recorded on a SPEX F-112 fluorescence spectrophotometer. Samples were contained in 1 cm x 1 cm quartz cuvettes, and the optical density was adjusted to approximately 0.1 at the excitation wavelength. Emission quantum yields are reported relative to perylene ($\Phi_{em} = 0.94$)$^{107}$ and appropriate correction was applied for the difference in refractive indices in the sample and actinometer solvent.$^{108}$ Time-resolved emission decays were obtained by time-correlated single photon counting on an instrument that was constructed in-house. Excitation was effected by using a violet diode laser (IBH instruments, Edinburgh, 405 nm, pulse width 800 ps). The time-resolved emission was collected using a red-sensitive, photon counting PMT (Hamamatsu, R928) and the light was filtered using 10 nm band-pass interference filters. Lifetimes were determined from the observed decays with the DAS6 deconvolution software (IBH Instruments, Edinburgh, Scotland). GPC was performed using a Rainin Dynamax model SD-200 solvent delivery system equipped with two PL-Gel 5 micron Mixed D columns (Polymer Laboratories, Inc., Amherst, MA) connected in series, and a UV detector set at a wavelength where the polymer absorbs.
Molecular weight information was calculated from the chromatograms using Polymer Laboratories software.

**Generation of the T3 and Ph-T3 Radical Cations**

These species were generated by photo-induced electron transfer from the neutral molecules to methyl violegen (MV$^{2+}$). To a 15 mM solution of MV$^{2+}$ in THF/acetonitrile (2:1) T3 or Ph-T3 were added until the absorbance of the analyte at 355 nm was 0.7. The solution was subjected to 10 mJ, 355 nm laser pulses to generate the cation radical. The differential absorption spectrum of the cation radical was recorded on an instrument built in-house.

**Radiation Techniques**

This work was carried out at the Brookhaven National Laboratory Laser-Electron Accelerator Facility (LEAF). The facility has been described elsewhere.$^{109,110}$ The electron pulse (≤ 120 ps duration) was focussed into a quartz cell with an optical path length of 20 mm containing the solution of interest. For the polymer solutions, the concentration of repeat units used was typically 0.2 – 2 mM. The monitoring light source was a 75 W Osram xenon arc lamp pulsed to a few hundred times its normal intensity. Wavelengths were selected using either 40 nm or 10 nm band pass interference filters. Transient absorption signals were detected with either FND-100Q silicon (≤ 1000 nm) or GAP-500L InGaAs (≥ 1100 nm) diodes and digitized with a Tektronix TDS-680B oscilloscope. The transmission/time data were analysed with Igor Pro software (Wavemetrics). Reaction rate constants were determined using a non-linear least squares fitting procedure described previously.$^{112}$ This procedure accounts for geminate recombination, which is encountered on the time scales investigated. Bimolecular rate constants were determined using the linearity of the observed pseudo-first order growth
of the product with respect to the solute concentration. Where not stated, uncertainties are +/- 15%. Bimolecular reactions of PAE ions with charge acceptors often went to completion with no detectable PAE$^{+\bullet}$ remaining. But in others, including most reactions with terthiophene, the kinetics proceeded to equilibria in which substantial fractions of the PAE$^{+\bullet}$ remained. The equilibrium constants could be calculated using this information. Molar extinction coefficients of the radical cations were calculated using $G(DCE^{+\bullet}) = 0.68$, where $G$ is the radiation chemical yield (molecules produced/100 eV). For the anions the reported $G$–values for the electron in THF has varied greatly. The value used was $G(e^{-}_{THF}) = 0.53$, the average of a number of reported values.

The total dose per pulse was determined before each species of experiments by measuring the change in absorbance of the electron in water. The dose received was calculated using $\varepsilon (\lambda = 700 \text{ nm}, e^{-}_{aq}) = 18,830 \text{ M}^{-1} \text{ cm}^{-1}$ and $G(e^{-}_{aq}) = 2.97$. The dose was corrected for the difference in electron density of the organic solvents used compared to that of water. Radiolytic doses of 5 – 18 Gy were employed. For the DCE/toluene solutions, dissolved oxygen was removed by purging with argon gas for at least 10 minutes, and subsequently sealing the cells with septa and parafilm. Solutions in THF were prepared in an argon environment and sealed under argon with Teflon vacuum stoppers. Samples were prepared immediately prior to use. During irradiation, samples were exposed to as little UV light as possible to avoid photodecomposition, although no evidence of this occurring was found within the time frames monitored. Measurements were carried out at 21° C.
CHAPTER 3
MECHANISM AND DYNAMICS OF TRIPLET TRANSPORT IN PLATINUM CONTAINING POLY (PHENYLENE ETHynyLENE)S

Introduction

A great deal of effort has been placed into investigating the carrier properties of singlet excitons in single chain conjugated polymers.\textsuperscript{17,66,71,73-75,87,120,121} However, despite these efforts, relatively little is known about the analogous properties of triplet excitons in these systems. This chapter describes a study aimed at investigating the properties and dynamics of triplet transport in platinum containing PPEs, often called Pt-acetylides.\textsuperscript{43,122} The major aim of the study is to determine whether or not intrachain energy transfer in Pt-acetylides is an efficient process. Another goal is to establish a model for transport in these materials that explains why this is or is not so.

The polymers used in this study are depicted in Figure 3-1. These polymers feature a Pt-acetylide backbone based on 1,4-diethynyl benzene as the acetylide unit. The 2,5-diethynyl thiophene unit was incorporated into the polymers at various loadings to serve as a trap for phenylene based triplets. Platinum acetylides were chosen because their triplet states are highly phosphorescent, and are thus easily monitored by photoluminescence spectroscopy.\textsuperscript{37-39} Furthermore, they posses a rigid rod “molecular wire” structure, and are easily synthesized by use of copper iodide catalyzed Hagihara condensation polymerization.\textsuperscript{44,122-124} In order to study the transport in these materials, thiophene was chosen as an energy trap. The conditions for a triplet energy trap are that
the triplet state of the trap must have a lower energy than the triplet state of the polymer main chain. In this case, the energy of the thiophene triplet is known to be 2.0 eV, while that of the phenylene triplet is 2.4 eV. In addition, varying the amount of thiophene in the reaction feed allows for straightforward synthesis of a series of copolymers in which the ratio of co-monomers varies.

![Chemical Structure](image)

\[
\begin{align*}
\text{P} & = 1, \quad y = 0 \quad \text{P}_{100T_0} \\
\text{P} & = 0.95, \quad y = 0.05 \quad \text{P}_{95T_5} \\
\text{P} & = 0.85, \quad y = 0.15 \quad \text{P}_{85T_{15}} \\
\text{P} & = 0.75, \quad y = 0.25 \quad \text{P}_{75T_{25}} \\
\text{P} & = 0, \quad y = 1 \quad \text{P}_{0T_{100}}
\end{align*}
\]

Figure 3-1. Structure of polymers featured in this chapter.

Unlike the polymers described in Chapter 2, which feature trap sites only at the end of the polymer chain, the polymers described in this chapter have trap sites dispersed throughout their backbone. There are several reasons for this change in approach. First, the synthetic challenges associated with end-capping conjugated polymers proved to be considerable. However, synthesis of the co-monomers used to make the polymers depicted in Figure 3-1 is fairly straightforward, and the associated polymerization reactions are also fairly simple and do not require a great deal of optimization.

Also, although the end-capping approach may seem somewhat more elegant than a random copolymerization, there is no difference in the resulting systems with respect to carrier transport. Migration along the copolymer chain is a one dimensional random-walk, meaning that a carrier does not move directly to the nearest trap. Instead, a carrier on a monomer unit that is far from a trap site has an equal probability of migrating to
either adjacent monomer, regardless of weather this brings the carrier nearer or further from the trap. Therefore, the number of monomer units that a carrier migrates through before reaching a trap site does not directly depend on the carrier’s distance from that site.

In addition, the distance between a carrier and a trap is not well defined even in an end-capped polymer because of the polydispersity inherent in synthetic polymers. Polydispersity relates to the distribution of molecular weights, and thus chain lengths, in a polymer sample. The higher the polydispersity, the greater the variety in chain lengths. For reference, any well-defined molecule has a polydispersity equal to 1. All conjugated polymers are synthesized by step condensation polymerizations, and the theoretical polydispersity of such processes approaches 2 as the functional group conversion approaches 100%. Practical polydispersities in conjugated polymers are often much higher because functional group conversion is less than quantitative. While fractionation of the polymer can help the situation somewhat, conjugated polymers are nonetheless quite polydisperse. Thus, the distance between an exciton and a trap is ill-defined regardless of whether the traps are incorporated into the polymer as end-caps or randomly in the backbone. Since this is so, the end-capping strategy does not offer any significant advantages over randomly incorporated traps. Therefore the latter method, which is much easier synthetically, was utilized in this study.

**Results and Discussion**

**Polymer Synthesis and Structural Characterization**

The chemical structures of the polymers which are the focus of this work are presented in Figure 3-1. The nomenclature adopted for the polymers is PₓTᵧ where x and y are the mole fraction of phenylene and thiophene monomers, respectively, used in the polymerization reactions.
It was originally envisioned that the polymers in this study would be prepared by the CuI catalyzed coupling of appropriate amounts of 2,5-diethynyl thiophene and 2,4-diethynyl benzene with bis(tributylphosphine)palladium dichloride. However, 2,5-diethynyl thiophene proved, in our hands, to be unstable to the polymerization conditions. Since bis(trimethylsilylethynyl) thiophene exhibits excellent stability under the polymerization conditions, it was deprotected *in situ* using tetrabutyl ammonium fluoride in the presence of copper (I) iodide and one equivalent of Pt(PBu₃)Cl₂ under Hagihara conditions to afford P₀T₁₀₀. This synthetic route is detailed in Figure 3-2.

![Figure 3-2. Synthesis of intermediate 3 and P₀T₁₀₀.](image)

The synthesis of the copolymers P₇₅T₂₅, P₈₅T₁₅, and P₉₅T₅ proved to be somewhat more challenging, as *in situ* deprotection of 2,5-bis(trimethylsilylethynyl) thiophene (2) in the presence of copper iodide and tetrabutylammonium fluoride with appropriate amounts of bis(tributylphosphine) platinum (II) chloride and 1,4-diethynylbenzene gave only low molecular weight material. In previous work, platinum containing PPE oligomers were synthesized using diplatinated diethynylbenzene and the resulting acetylides, featuring monochlorinated platinum end-groups, were then used in further Hagihara coupling reactions. This methodology was extended to thiophene based
monomers by deprotecting 2 in situ with tetrabutyl ammonium fluoride in the presence of CuI and an excess of Pt(PBu₃)₂Cl₂ to afford compound 3 (see Figure 3-2), which is very stable and can be easily purified by chromatography. Thus 3 was used in a three component A-A + A’-A’ + B-B polymerization with appropriate amounts of 1,4-diethynyl benzene, Pt(PBu₃)Cl₂ and CuI gives copolymers P₉₅T₅, P₈₅T₁₅, and P₇₅T₂₅, as shown in Figure 3-3.

Note that unlike the end-capping polymerizations discussed in Chapter 2, these polymerizations were performed under conditions where the end-group stoichiometry was balanced. That is, each polymerization featured an equal molar quantity of chloroplatinum and terminal acetylene functionalities. Any stoichiometric imbalances give only low molecular weights, as predicted by the classic equation of Carothers.₁²⁵,₁²⁶

\[
x \cdot 3 + (1-x) \quad \text{PtClCl} + \quad \text{Cul, toluene/DIPA} \quad \text{R.T. 24 hrs} \quad \text{P₉₅T₅} (x = 0.05, y = 0.95) \\
\text{P₈₅T₁₅} (x = 0.15, y = 0.85) \\
\text{P₇₅T₂₅} (x = 0.25, y = 0.75)
\]

Figure 3-3. Synthesis of platinum containing phenylene-thiophene copolymers.

The copolymers feature a platinum-phenyleneacetylide backbone in which varying amounts of thiophene are substituted for phenylene. Because the thiophene moieties in the backbone orient their substituents at the 2 and 5 position at angles somewhat less than 180°, these polymers are not expected to be completely linear, however, they should nonetheless adopt a rather extended conformation in solution. The synthetic design, where thiophene is introduced only via the diplatinated compound 3 prevents “blocks” of adjacent thiophene units in the copolymer, since the reactive termini of 3 cannot couple with one another. The only possible reaction of 3, in this system, is coupling with diethynyl benzene. Thus there is no possibility that any of the photophysical results
presented herein are the product of very low energy trap sites involving multiple adjacent thiophene units.

The molecular weights of these polymers vary greatly. However, this is unimportant for the purposes of this study which is not concerned with behaviors of the bulk materials. Furthermore, the level of thiophene incorporation does not depend on the molecular weight of the polymers, but on the thiophene loading. Thus, carrier transport from the phenylene main-chain to a thiophene trap-site, the property of interest here, does not depend on molecular weight.

$^1$H NMR is particularly instructive in elucidating the structure of these polymers. The aromatic region of the polymer’s proton NMR is presented in Figure 3-4. The phenylene moieties in $\text{P}_{100} \text{T}_0$ show resonances at 7.1 ppm, and are clearly distinct from the thiophene resonances in $\text{P}_0 \text{T}_{100}$, which appear at 6.5 ppm. On this basis, it is possible to assign the aromatic resonances in the copolymers and compare the integration of thiophene to phenylene protons in order to determine the exact composition of the polymer.$^{127}$ The ratio of thiophene to phenylene in $\text{P}_{95} \text{T}_5$, $\text{P}_{85} \text{T}_{15}$, and $\text{P}_{75} \text{T}_{25}$ is calculated to be 1:30, 1:13, and 1:8, as compared to the theoretical values of 1:19, 1:6 and 1:4, respectively. Thus, approximately half the amount of thiophene in the feed is actually incorporated into the polymers. This suggests that thiophene monomer 3 is somewhat less reactive to Hagihara coupling than $\text{Pt(PBu}_3)_2\text{Cl}_2$. This observation may also explain why the copolymers exhibit lower molecular weights in comparison to the homopolymers.
Figure 3-4. Aromatic region of the polymers $^1$H NMR spectra. From top to bottom, the spectra are $P_{100}T_0$, $P_{95}T_5$, $P_{85}T_{15}$, $P_{75}T_{25}$, and $P_0T_{100}$. The resonance at 7.26 ppm corresponds to the solvent (chloroform).

It is important to note that the thienyl protons give relatively sharp resonances in the NMR. This indicates that all thiophene moieties are in essentially identical magnetic environments. Thus, the thiophene comonomers are randomly distributed along the
polymer backbone and the evidence shows no sign of blocks or regions on the polymer chains with a high localized concentration of thiophene units.

**Photophysical Mesurements**

**Absorption and emission spectroscopy**

The absorption spectra of the polymers used in this study are presented in Figure 3-5, and their photophysical characteristics are summarized in Table 3-1. First the spectra of the homopolymers, P\textsubscript{100}T\textsubscript{0} and P\textsubscript{0}T\textsubscript{100}, is considered. Each of these spectra exhibit one broad, featureless band with $\lambda_{\text{max}}$ at 341 nm and 402 nm, respectively. This band is assigned to the long-axis polarized absorption of each polymer.

The copolymers show more complex spectra. The absorption of P\textsubscript{95}T\textsubscript{5} is dominated by a broad band with $\lambda_{\text{max}}$ at 347 nm. This band is at nearly identical in shape and wavelength to the absorption of the all-phenylene polymer, and as such it is assigned to absorption of a phenylene based chromophore. In addition to the main band, a shoulder at 402 nm appears in this spectrum. Because its energy is similar to that of the thiophene homopolymer, this band is assigned to absorption of a thiophene based chromophore. The spectrum of P\textsubscript{85}T\textsubscript{15} shows the same two bands, except that the relative intensity of the thiophene-based (402 nm) absorption is greater for this polymer than in P\textsubscript{95}T\textsubscript{5}. This corresponds with expectation, given the increased level of thiophene loading in P\textsubscript{85}T\textsubscript{15}.

A broad band centered at 375 nm is the major feature in the absorption spectrum of P\textsubscript{75}T\textsubscript{25}. This band is red-shifted with respect to the dominant absorptions of P\textsubscript{95}T\textsubscript{5} and P\textsubscript{85}T\textsubscript{15}. A shoulder at 402 nm is also present in this spectrum. However, the dominant band ($\lambda_{\text{max}} = 375$) is so broad as to encompass nearly the entire shoulder.
Figure 3-5. Absorption spectra of polymers in THF solution.

Table 3-1. Summarized absorption and photoluminescence data.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Abs. $\lambda_{\text{max}}$ / nm</th>
<th>Photoluminescence $\lambda_{\text{max}}$ / nm</th>
<th>$\Phi^F$</th>
<th>$\Phi^P$</th>
</tr>
</thead>
<tbody>
<tr>
<td>P$_{100}$T$_0$</td>
<td>341</td>
<td>----</td>
<td>514</td>
<td>----</td>
</tr>
<tr>
<td>P$_{95}$T$_5$</td>
<td>347</td>
<td>420</td>
<td>604</td>
<td>0.002</td>
</tr>
<tr>
<td>P$<em>{85}$T$</em>{15}$</td>
<td>347</td>
<td>420</td>
<td>604</td>
<td>0.063</td>
</tr>
<tr>
<td>P$<em>{75}$T$</em>{25}$</td>
<td>375</td>
<td>420</td>
<td>604</td>
<td>0.053</td>
</tr>
<tr>
<td>P$<em>0$T$</em>{100}$</td>
<td>402</td>
<td>420</td>
<td>604</td>
<td>0.057</td>
</tr>
</tbody>
</table>
The photoluminescence spectra of the homo- and copolymers are presented in Figure 3-6, and the results are also tabulated in Table 3-1. Photoluminescence lifetimes appear in Table 3-2. Each band is labeled as P or T, corresponding respectively to phenylene or thiophene based luminescence. Additionally, the subscripts F or P designate fluorescence and phosphorescence, respectively.

The room temperature spectra, beginning with the homopolymers, will be considered first. P$_{100}$T$_0$ exhibits very weak emission between 400 – 500 nm which is assigned as fluorescence on the basis of previous investigations.$^{44,128}$ In addition, this polymer shows moderate emission centered at 514 nm. This band exhibits a very long lifetime (Table 3-2), and is completely quenched in the presence of oxygen. On this basis, and because of its similarity to previously published spectra of structurally similar oligomers,$^{44}$ the emission centered at 514 nm is assigned as phosphorescence.

P$_0$T$_{100}$ also shows two emission bands, one centered at 420 nm, and the other centered at 604 nm. The 604 nm band is completely quenched in an air-saturated solution, and has a lifetime of several microseconds (Table 3-2). This band is therefore assigned as phosphorescence. The band at 420 nm is not quenched by oxygen and has a lifetime less than 5 ns. The 420 nm band is therefore assigned as fluorescence. These assignments agree with previously reported data on similar materials.$^{36}$
Figure 3-6. Photoluminescence spectra of polymers in argon saturated solutions of THF (room temperature) and 2-methyl THF (78 K). Solid lines: room temperature, dashed lines: 78 K. Note that the room temperature spectra are normalized to the fluorescence band when applicable, while the low-temperature spectra are normalized to the strongest phosphorescence band.
Table 3-2. Photoluminescence rate and lifetime information.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>514 nm</th>
<th>605 nm</th>
<th>298 K</th>
<th>605 nm</th>
<th>298 K</th>
<th>78 K</th>
<th>605 nm</th>
<th>78 K</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>k / s⁻¹</td>
<td>τ / µs</td>
<td>k / s⁻¹</td>
<td>τ / µs</td>
<td>k₁ / s⁻¹</td>
<td>k₂ / s⁻¹</td>
<td>τ₁ / µs</td>
<td>τ₂ / µs</td>
</tr>
<tr>
<td>P₁₀₀T₀</td>
<td>5.4 x 10⁴</td>
<td>18</td>
<td>----</td>
<td>----</td>
<td>6.0 x 10⁵</td>
<td>----</td>
<td>----</td>
<td>----</td>
</tr>
<tr>
<td>P₉₅T₅</td>
<td>1.7 x 10⁵</td>
<td>5.3</td>
<td>1.1 x 10⁶</td>
<td>9.1</td>
<td>1.4 x 10⁹</td>
<td>2.1 x 10⁴</td>
<td>8.8 x 10⁴</td>
<td>2.8 x 10⁴</td>
</tr>
<tr>
<td>P₈₅T₁₅</td>
<td>3.0 x 10⁶</td>
<td>3.3</td>
<td>3.1 x 10⁶</td>
<td>7.7</td>
<td>3.6 x 10⁹</td>
<td>4.2 x 10⁴</td>
<td>9.0 x 10⁴</td>
<td>2.6 x 10⁴</td>
</tr>
<tr>
<td>P₇₅T₂₅</td>
<td>7.1 x 10⁵</td>
<td>1.4</td>
<td>1.4 x 10⁵</td>
<td>7.1</td>
<td>5.7 x 10⁹</td>
<td>----</td>
<td>4.4 x 10⁵</td>
<td>----</td>
</tr>
<tr>
<td>P₀T₁₀₀</td>
<td>----</td>
<td>----</td>
<td>1.8 x 10⁴</td>
<td>5.6</td>
<td>----</td>
<td>6.4 x 10⁵</td>
<td>----</td>
<td>----</td>
</tr>
</tbody>
</table>

Now turning to the copolymers, P₉₅T₅ exhibits a very weak band at 420 nm that is not quenched by oxygen. This band is assigned to thiophene-based fluorescence. A band at 514 nm, corresponding to phenylene based phosphorescence, is also apparent. However, this band is quite weak (< 5% of the total phosphorescence). Instead, a band centered at 605 nm, corresponding to thiophene phosphorescence, dominates the spectrum. The emission spectra of P₈₅T₁₅ and P₇₅T₂₅ both feature a strong band at 420 nm, which, based on comparison to the all-thiophene polymer, corresponds to thiophene-based fluorescence. No emission centered at 514 nm, corresponding to phenylene phosphorescence, is readily apparent in either of these polymers. Time resolved studies (see below) show that the phenylene-based phosphorescence at 514 nm is present, but is so weak as to be buried under the “tail” of the fluorescence. In fact, the only phosphorescence that is readily apparent in these copolymers is centered at 605 nm, corresponding to emission from a thiophene-based luminophore.

These results are quite remarkable. The lack of phenylene based (514 nm) phosphorescence in P₈₅T₁₅ and P₇₅T₂₅ indicates efficient energy transfer from the phenylene main-chain to the thiophene “traps” along the chain. Even when the
concentration of thiophene is less than 5%, (P₉₅T₅), energy transfer is more than 95% efficient, based on the relative intensities of the phenylene and thiophene emission.

Trends in the phosphorescence lifetimes of the copolymers support this idea. At room temperature, P₁₀₀T₀ exhibits a phosphorescence lifetime (τ) of 18 µs, whereas P₀T₁₀₀ displays τ = 5.6 µs. The copolymer lifetimes (Table 2) at room temperature show a distinct trend. As the thiophene concentration increases, τ of both the phenylene and thiophene components of the emission decreases. If the two excited states were not coupled in equilibrium, but were instead related to two independent chromophores, the lifetimes would not be expected to show any significant change with increased loading of thiophene.

The photoluminescence spectra of the copolymers changes significantly at low temperature. Whereas thiophene-based phosphorescence dominates the triplet-emission at room temperature for all of the copolymers, at 78 K the phosphorescence of P₉₅T₅ and P₈₅T₁₅ is dominated by phenylene-based phosphorescence. Thus, decreasing the temperature dramatically decreases the efficiency of energy transfer in polymers with lower thiophene loadings. This effect is not seen at higher loadings of thiophene, as evidenced by the low temperature emission of P₇₅T₂₅. In this polymer, the spectrum is dominated by thiophene-based emission even at low temperatures.

**Phosphorescence quenching**

The phosphorescence of P₁₀₀T₀ and P₀T₁₀₀ are quenched by addition of methyl viologen (N,N’ dimethyl-4,4’-bipyridinium, MV²⁺). Stern-Volmer analysis of these polymers gives quenching constants (Ksv) of 3.9 x 10⁵ for P₁₀₀T₀ and 6.7 x 10⁵ for P₀T₁₀₀. Considering the phosphorescence lifetimes, these constants correspond to a purely diffusion controlled (dynamic) quenching process.
The quenching behavior of P$_{95}$T$_5$ was also explored, and the results are presented in Figure 3-7. P$_{95}$T$_5$ was used for these experiments because it is the only copolymer for which both phenylene and thiophene based phosphorescence is readily observable at room temperature. These experiments show quenching constants for the phenylene and thiophene components of the phosphorescence that are essentially identical to those in the corresponding homopolymers.

Figure 3-7. Stern-Volmer quenching of P$_{95}$T$_5$ in THF solution. The uppermost spectrum has [MV$_2^+$] = 0 µM, and the concentration of MV$_2^+$ increases by 1 µM in each subsequent spectrum. The insert shows the linear portion of the Stern-Volmer plots for the phenylene (530 nm, circles) and thiophene (614 nm, triangles) portions of the spectra.

These results again imply that the phenylene and thiophene based triplets are coupled in a dynamic equilibrium. If this were not the case, and the phosphorescence of P$_{95}$T$_5$ was a result of thiophene and phenylene based triplet states that did not interconvert, then the results would be expected to be much different. Recall that results from quenching experiments with the homopolymers show that MV$_2^+$ can effectively
quench both phenylene and thiophene phosphorescence, and both processes are diffusion controlled. Thus, in the absence of an equilibrium system, it would be expected that the thiophene-based emission would be quenched preferentially to the phenylene-based emission because, as evidenced by the photoluminescence spectrum, there is a much larger concentration of thiophene triplets than phenylene triplets in the polymer chain.

**Transient absorption spectroscopy**

Figure 3-8 shows the time-resolved transient absorption spectra of the polymers. In the homopolymers, the major feature is a broad transient absorption centered at 6100 nm in $P_{100}T_0$, and around 640 nm in $P_0T_{100}$. These bands are assigned to the triplet-triplet ($T_1 \rightarrow T_n$) absorption of the polymers.

The transient absorption of the three copolymers are quite similar. All are dominated by a broad absorption centered at 630 nm, intermediate between the all-phenylene and all-thiophene homopolymers. The shape the bands are essentially identical for all three of the copolymers. However, there is a more subtle, yet noteworthy, component of the transient absorption spectra. Specifically, close examination of the negative intensity band due to ground state bleaching reveals an interesting trend. This feature does not mirror the ground state absorption, but instead shows a continuous red-shift with increasing thiophene concentration across the series.
Figure 3-8. Triplet-state transient absorption spectra. The most intense spectrum were obtained immediately after photoexcitation with a 10 mJ, 355 nm laser with a 10 ns pulse width. Each subsequent spectrum was obtained 1 µs after the preceding spectrum. The dashed vertical line is at 350 nm.

**Time resolved emission**

Time resolved photoluminescence spectroscopy was applied to P$_{95}$T$_5$ in order to gather information about energy transfer in this polymer. The results, as shown in Figure 3-9, show that while the phenylene phosphorescence (514 nm) is complete within about 5 µs, the thiophene (605 nm) phosphorescence is still present after more than 30 µs. This
observation supports the notion that energy is being transferred from a phenylene-based state to a thiophene-based state.

In order to gain any information about energy transfer, it would be necessary to deconvolute the decay curves into two components: one corresponding to phosphorescence and the second corresponding to energy transfer. However, at room temperature, the decay at both 514 nm and 605 nm is described by a single exponential equation. This precludes any such analysis.

Figure 3-9. Time resolved emission spectrum of P$_{95}$T$_5$ in THF solution at room temperature, excitation wavelength 355 nm. Inset: Normalized emission decay at 514 nm (circles) and 605 nm (triangles)

The large changes that were observed in the phosphorescence spectra at low temperatures indicated the possibility that at 78 K energy transfer might be slowed
sufficiently as to allow for observation of the process. Indeed, at low temperatures, two decay components were observed in the decay of both the phenylene and thiophene phosphorescence of P₉₅T₅ and P₆₅T₁₅. Figure 3-10 presents the normalized phenylene (514 nm) and thiophene (605 nm) decays in P₉₅T₅. This data is further summarized in Table 3-2.

![Normalized emission decay of P₉₅T₅ at 78 K. The dashed line represents phenylene (514 nm) decay and the solid line represents thiophene phosphorescence decay (605 nm).](image)

The phenylene-based phosphorescence decay in P₉₅T₅ is dominated by a fast component (k = 1.4 x 10⁶ s⁻¹). This decay is far too fast to relate to phosphorescence, based on comparison with the homopolymers. It must therefore be associated with energy transfer to thiophene. If this is true, increasing the loading of thiophene should increase
the rate of the short decay component. This prove to be the case, as demonstrated by the results on P85T15, the 514 nm emission decay of which features an energy transfer component that is faster than in P95T5. However, the phenylene-based phosphorescence decay in P75T25 is unlike that in the copolymers with lower concentrations of thiophene in that it is monoexponential. This implies that transport in this polymer is too fast to be measured. This phenomenon is discussed in detail below.

Note that the thiophene-based (605 nm) phosphorescence is also biexponential in both P95T5 and P85T15. The minor component of both of these decays corresponds well to the phosphorescence decay of the phenylene-based emission (514 nm). Careful inspection of the steady-state spectra reveal that there is some residual phenylene-based phosphorescence even at 605 nm. This residual phenylene phosphorescence likely accounts for the minor component of the 605 nm emission decay.

General Discussion

Electronic model

In addition to providing information about the structure of the polymers, the ¹H NMR spectra provide useful information about the influence of thiophene doping on the phenylene-based polymer chains (Figure 3-4). When thiophene is introduced into the polymer chain new resonances corresponding to thiophene protons appear in the NMR. In addition a change is observed in the resonances associated with phenylene protons. Specifically, a new resonance at 7.1 ppm, which is not present in P100T0, appears in the ¹H NMR spectra of the copolymers. The ratio of the relative integration of this new resonance and the thiophene resonance is 4:1. Noting that each thiophene has two protons and each phenylene four, the resonance at 7.1 ppm can be assigned to the phenylene moieties adjacent to thiophene. This assignment makes sense, considering that
the electron-releasing thiophene ring would be expected to cause an upfield shift on nearby groups. Importantly, this result shows that even in the ground state, the electron-releasing effects of thiophene perturb nearby phenylene moieties.

This information, considered in light of previous work showing that the singlet excited state of Pt containing PAE’s is delocalized over approximately five to seven arylene units allows for the construction of a model to explain the excited states of these polymers. The cartoon in Figure 3-10A provides an illustration of the effects of a single thiophene trap in a Pt-acetylide chain composed of phenylene-based. For the purposes of this discussion, the delocalization of the singlet excited states is taken to be five repeat units. In this depiction, the dark circle represents thiophene and the light circles represent phenylene. The grey circles represent phenylene moieties that are within one chromophore length of a thiophene moiety. Note a single thiophene unit perturbs its “nearest neighbor” and “second-nearest neighbor”. In this case, it would be expected that an initial excitation created within one chromophore length of a thiophene unit (ie. on the black or grey circles in 3-10A), would undergo ultra-fast transport in the singlet to the thiophene trap. An exciton created elsewhere on the chain (the white circles in 3-10A) may migrate to the trap either as a singlet or a triplet (vide infra).

Figure 3-10B considers the case where the concentration of thiophene is somewhat higher, in this case one in five. Although the individual chromophores in this case are identical to those in a polymer with more dilute thiophene loading, here every phenylene is either a “nearest neighbor” or “second-nearest neighbor” to a thiophene. Thus, every phenylene unit is within one chromophore length of a thiophene. In this case, any exciton on the chain is with one chromophore length of a thiophene trap. Thus, it would
be expected that the system can be described by ultra-fast singlet transport within a single chromophore. Importantly, because transport is much faster in the singlet state as compared to the triplet state, triplet transport is not expected to play a role in this scenario.

Figure 3-11. Schematic representation of platinum acetylide polymers with low (A) and high (B) levels of thiophene incorporation. The dark circles represent thiophene monomers, and the light circles represent phenylene monomers. The grey circles represent phenylene units that are within one chromophore length of a thiophene moiety.

The absorption spectra (Figures 3-5) are easily understood in light of this model. The shoulder in the absorption spectra of P$_{95}$T$_5$ and P$_{85}$T$_{15}$, previously assigned to thiophene-based absorption, accounts for a disproportionately high amount of the total absorption in these cases if only the concentration of thiophene in the backbone is considered. Recall that P$_{95}$T$_5$ contains only 1 thiophene in about every 30 repeat units, or about 3% of the total number of repeat units. However, the shoulder centered at 402 nm, previously assigned to thiophene based absorption, accounts for roughly 10% of the total absorption in this polymer. Taking into account that each thiophene is actually part of a
chromophore that contains four nearby phenylene units, then this apparent contradiction becomes clear, since the thiophene-based chromophores actually include not one but 4 out of every 30 (or about 10%) of the arylene units in the polymer. The spectrum of P_{85T15} can be explained in the same fashion. Here, the thiophene-based absorption accounts for about 30% of the total absorption of the polymer. This is consistent with expectation considering that the thiophene-to-phenylene ratio is about three times higher than in P_{95T15}.

The model also accounts for red-shift in the absorption of P_{75T25}. This polymer, featuring the highest loading of thiophene among the copolymers, is best explained by considering that the concentration of thiophene is high enough that it is approaching the regime in depicted in Figure 3-10B. In this polymer, nearly every phenylene is perturbed by a nearby thiophene. Thus, the major absorption band is neither phenylene-based nor is it completely thiophene-based.

Careful examination of the triplet-triplet transient absorption spectra (Figure 3-8) is useful in explaining the triplet state of these materials. Note that the copolymers all feature a single, broad triplet-triplet absorption centered at 610 nm, intermediate between the absorptions of the all-phenylene and all-thiophene homopolymers. This means that the lowest energy triplet cannot be described as being localized on thiophene alone. A more reasonable description of the lowest energy triplet state in the copolymers is a thiophene-based chromophore that is perturbed the nearby phenylene moieties. That the absorption is essentially identical for all of the copolymers, regardless of thiophene loading, implies that the lowest energy triplet states of all of the copolymers are also identical. In other words, the lowest energy triplet is mostly localized on thiophene, but it
“leaks” slightly onto the adjacent phenylene units. This is consistent with previous work that showing that the triplet state is highly localized.\textsuperscript{44}

More subtly, the negative intensity “bleach” of the ground states in the transient absorption does not mirror the absorption spectra. In fact, while all of the ground states show strong absorption at 350 nm, in the transient absorption (dashed line), there is little to no ground state bleaching at this wavelength. In fact, the ground state bleaching in the transients are focused at the low energy end of the ground state absorption. This indicates that the triplet state is dominated by thiophene-based chromophores, even when the concentration of thiophene in the polymer backbone is low.

The photoluminescence data (Figure 3-6) are consistent with a model where the singlet is somewhat delocalized and the triplet is highly localized. The room temperature photoluminescence features highly efficient energy transfer from the phenylene-based main chain to the thiophene-based trap sites. At low temperature, a significant portion of energy transfer can be eliminated, thus enabling observation of the situation when energy transfer between chromophores is incomplete. Thus at 78 K $P_{95T_5}$ and $P_{85T_{15}}$ each show a mixture of phenylene and thiophene based phosphorescence. This observation fits with expectations, considering Figure 3-10A.

On the other hand, the photoluminescence of $P_{75T_{25}}$ does not change significantly at low temperature. This is expected if $P_{75T_{25}}$ can be modeled by Figure 3-10B, where every chromophore contains a thiophene. In this case, all of the energy transfer would be expected to occur within a single chromophore in the singlet state, and thus be fast even at low temperatures. This bears out in the results; $P_{75T_{25}}$ does not exhibit any significant phenylene based emission, even at low temperatures.
Kinetics and mechanism of energy transport

Having reached an understanding of the nature of the excited state, it is also possible to examine the kinetics of energy transport. Time resolved emission experiments are useful to this end. Transport at room temperature proved too fast to observe, thus the most interesting experiments focused on studying the polymers at 78 K. Furthermore, it is only expected that triplet transport could be observed in polymers with a dilute loading of thiophene, P\textsubscript{95}T\textsubscript{5} and P\textsubscript{85}T\textsubscript{15}. Transport in P\textsubscript{75}T\textsubscript{25} is expected to occur only in the singlet state for reasons explained above.

At 78 K, the phenylene phosphorescence decay (Figure 3-9) has two components. The rate of the fast component (Table 3-2) is too slow for singlet energy transfer, which is expected to occur on the picosecond timescale,\textsuperscript{61} but is clearly much faster than the rate of phosphorescence based on comparison with the phosphorescence lifetime of P\textsubscript{100}T\textsubscript{0}. It is therefore reasonable to conclude that this fast component of the decay corresponds to energy transfer in the triplet state.

If the assignment of the fast decay component at 514 nm to triplet transfer is correct, then this rate constant should increase as the loading of thiophene increases. This is indeed the case. P\textsubscript{85}T\textsubscript{15} features a thiophene concentration 2.3 times greater than P\textsubscript{95}T\textsubscript{5}, based on \textsuperscript{1}H NMR integration. The fast component of the 514 nm emission decay, which corresponds to triplet energy transfer, is 2.6 times faster in P\textsubscript{85}T\textsubscript{15} than in P\textsubscript{95}T\textsubscript{5}, which agrees remarkably well with expectation. When the loading of thiophene is high, as in P\textsubscript{75}T\textsubscript{25}, no triplet transport is observed. This is consistent with the notion that transport in this system occurs only in the singlet for copolymers with high thiophene loadings.
It is important to note that the slow components of the phenylene emission in P_{95T5} and P_{85T15} do not correspond to the actual rate of phenylene phosphorescence as observed in P_{100T0}. This indicates that while the observed rate constants are useful as approximate indicators of the energy transfer rates, they do not correspond to the actual rates of triplet energy transfer.\textsuperscript{129} Zimmerman et. al. showed that in a well-defined donor-bridge-acceptor system it is possible to obtain the exact rate constants by mathematical manipulation of the observed rate data.\textsuperscript{129} However, these polymers are ill-defined, and it is therefore impossible to treat these results in this fashion. Nonetheless, the observed results are excellent guidelines for obtaining a general understanding of the kinetics of this system.

Figure 3-12. Jablonki diagrams representing the all-triplet (A) and all-singlet (B) mechanisms for energy transfer. The subscripts P and T indicate phenylene and thiophene based excited states, respectively.

Energy transfer in platinum acetylide polymers can occur by two limiting mechanisms. These are depicted in Jablonski diagrams in Figure 3-11. Figure 3-11A depicts the all-triplet limit. In this case, the initial photoexcited state intersystem crosses
to a triplet very rapidly with respect to the rate of energy transport. The resulting triplet then migrates along the chain to a thiophene trap. In Figure 3-11B, the all-singlet mechanism is depicted. In this limit, the initial photoexcited state migrates to the trap site forming a thiophene singlet. The singlet then intersystem crosses at thiophene, resulting in a thiophene triplet.

The results seem to indicate that both mechanisms are operational. The fact that the P85T15 and P75T25 both show considerable thiophene-based fluorescence is a clear indicator that singlet state transport plays an important role. Importantly, this fluorescence is strong even when the excitation is at a wavelength where thiophene is not expected to absorb. For example, the photoluminescence spectra in Figure 3-6 were all obtained with a 350 nm excitation wavelength, where the absorption is dominated by phenylene-based chromophores. This observation supports the notion that singlet-state energy transfer occurs from an initially excited phenylene-based chromophore to the thiophene trap sites. However, at 78 K the observed energy transfer clearly occurs in the triplet, as discussed above. This leads to the somewhat surprising conclusion that at room temperature transport occurs primarily in the singlet state, despite the fact that the readily observable optical properties of platinum acetylides are dominated by triplet state photophysics. At 78 K the singlet-state pathway is less important, and transport occurs primarily in the triplet state.

**Conclusions**

A series of platinum containing PPEs with varying loadings of thiophene were synthesized by the Hagihara coupling methodology. The polymers were characterized by GPC and $^1H$ NMR. $^1H$ NMR confirmed both the relative phenylene and thiophene
content of the polymers, and provided some early hints as to the effects of the electron releasing thiophene groups on nearby phenylene moieties.

The triplet excited state of these polymers is delocalized over approximately five arylene rings. Rapid and efficient energy transfer from the phenylene based main-chain to the thiophene trap sites results in polymers where the vast majority of phosphorescence is thiophene-like, even when the thiophene loading is less than 5%. This energy transfer is slowed considerably at low temperatures, resulting in a mixture of phenylene and thiophene based emission in polymers with a low level of thiophene doping. Furthermore, the low-temperature phenylene-based phosphorescence decay can be deconvoluted into two components. The fast component relate to the rates of energy transfer, while the slow component relates to phosphorescence decay. As expected, the rate of energy transfer increases with increased thiophene loading.

It is impossible to directly correlate the experimentally observed decay rates to the actual energy transfer rates. However, it is clear that energy transport in the triplet state is important in platinum acetylide polymers, and that this process is competitive with phosphorescence. Nonetheless, it is reasonable to conclude that energy transfer in platinum acetylide polymers occurs in both the singlet and triplet excited states. Energy transfer is fast in the singlet state, and somewhat slower in the triplet state. The triplet excitation diffuses more slowly due to its spatially confined nature, and because coupling of the chromophore segments by exchange interactions is comparatively weak.

**Experimental Section**

**General Synthesis and Materials**

*trans*-Bis(tributylphosphine)palladium dichloride (Pd(PPh₃)₂Cl₂) and tetrakis(tributylphosphine)palladium were purchased from Strem Chemicals and used as
received. THF and 2-methyl tetrahydrofuran were purchased from Acros and distilled from sodium/benzophenone under argon before use. All other reagents and solvents were purchased from either Acros or Aldrich and used as received unless otherwise noted. $^1$H and $^{13}$C spectra were recorded on a Varian 300 MHz spectrometer. Column chromatography was preformed using silica gel (Merk, 230 – 400 mesh). Gel permeation chromatography (GPC) was preformed using a Rainin Dynamex model SD-200 solvent delivery system equipped with two PL-Gel 5 Mixed D columns (Polymer Laboratories, Inc., Amherst, MA) and a UV detector set at a wavelength where the polymer under investigation was known to absorb. Polymer molecular weight information was calculated using Polymer Laboratories software, and is reported relative to polystyrene standards. The synthesis and characterization of 1,4-diethynylbenzene and P$_{100}$T$_0$ has been discussed previously.$^{87,128}$

**Synthetic Procedures**

**2,5-Diiodothiophene (1)** To a flask containing a mixture of acetic acid and chloroform (14 mL, 3:4) was added thiophene (1.00 g, 11.9 mmol) and N-iodosuccinamide (NIS) (5.84 g, 24.4 mmol). The flask was covered, and the mixture stirred at room temperature for 16 hours. The reaction mixture was then washed with an aqueous solution of sodium thiosulfate (10%), and pure water. The organic phase was dried over MgSO$_4$ and the solvent was removed under reduced pressure. Column chromatography with hexanes afforded the desired product as a reddish solid. (yield 2.80g, 70%) $^1$H NMR (CDCl$_3$, 300MHz) $\delta$ 6.90(s, 2H); $^{13}$C NMR (CDCl$_3$, 300 MHz) $\delta$ 76.36, 138.65.
**Compound 2** To a flask charged with THF and diisopropylamine (DIPA) (8 mL, 1:1) was added 2,5-diodothiophene (668 mg, 2.0 mmol). The resulting solution was degassed for 30 min by spurring with argon. To this solution was added trimethylsilylacetylene (491 mg, 5 mmol), Pd(PPh₃)₄ (12 mg, 1.6 mmol), and copper iodide (4 mg, 2 mmol). The reaction was then stirred at room temperature for 24 hours. After this time the solvent was removed under reduced pressure. Flash chromatography of the residue with hexanes gave the desired product as a yellow solid. (yield 440 mg, 80%). ¹H NMR (CDCl₃, 300MHz) δ 0.24 (s, 18H), 7.04 (s, 2H); ¹³C NMR (CDCl₃, 300 MHz) δ -0.23, 96.86, 99.90, 124.47, 132.29.

**Compound 3** To a flask charged with Pt(PBu₃)₂Cl₂ (501 mg, 0.75 mmol) and 2 (69 mg, 0.25 mmol) in a mixture of toluene and piperidine (12 mL, 3:1) was added CuI (3 mg) and tetrabutylammonium fluoride (0.51 mL, 0.51 mmol). The reaction mixture was deoxygenated with argon spurring for 15 min. After stirring for 2 days at room temperature, the solvent was removed under reduced pressure. The resulting residue was stirred in dichloromethane, and the resulting suspension filtered. The soluble portion was collected and purified by flash chromatography with hexanes as the eluent to yield 3 as a yellow solid. (yield 224 mg, 64%). ¹H NMR (CDCl₃, 300MHz) δ 0.93 (t, J = 7.20Hz, 36H), 1.38-1.62 (m, 48H), 1.90-2.80 (m, 24H); ¹³C NMR (CDCl₃, 300 MHz) δ 13.76, 21.90(t, J = 66.30 Hz), 24.24(t, J = 27.9 Hz), 26.01, 88.26, 93.77, 126.84. ³¹P NMR (CDCl₃, 300 MHz) δ -1.68, 8.04, 17.77.

**P₉₅T₅** An ampoule charged with a mixture of diisopropylamine and toluene (3 mL, 1:5) with a small magnetic stirring bar was fitted with a septum and spurred with argon for five minutes. The ampoule was then subjected to vacuum for one minute by inserting
a needle connected by hoses to a water aspirator into the septum. This process was repeated twice, ending with argon-spurging. To the ampoule were rapidly added 3 (14 mg, 0.01 mmol) 1,4-diethynylbenzene (24 mg, 0.19 mmol) and CuI (2 mg, 0.01 mmol). The solution was degassed by three more argon-vacuum cycles, sealed under vacuum, and stirred at room temperature for 24 hours. After this time, the ampoule was broken and the solution was poured into 50 mL of methanol to induce precipitation of the polymer as a yellow solid. The desired polymer was collected by filtration and washed with methanol and then water. This solid was dissolved in a minimal amount of chloroform, precipitated again into methanol, and collected by filtration to yield the desired polymer as a yellow solid (yield 96 mg, 70%). $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 0.77-1.03 (br, 72H), 1.30-1.72 (br, 96H), 1.86-2.25 (br, 48H), 6.57-6.61 (s, 0.48H), 7.03-7.11 (d, 3.15H), 7.14-7.32 (m, 11.19H). GPC: $M_n = 4,570; M_w = 12,843$, PDI $=$ 2.81.

$P_{85T15}$ The same procedure used for $P_{95T5}$ was employed except the reagents used were as follows: 3 (47 mg, 0.03mmol), Pt(PBu$_3$)$_2$Cl$_2$ (105 mg, 0.16mmol), 1,4-diethynylbenzene (24 mg, 0.19mmol), and CuI (2 mg, 0.01 mmol). $P_{85T15}$ was obtained as a yellow solid (yield 99.10mg, 72%) $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 0.76-1.02 (m, 72H), 1.32-1.75 (m, 96H), 1.84-2.25 (m, 48H), 6.58-6.61 (s, 0.67H), 7.04-7.12 (m, 2.53H), 7.18-7.27 (m, 6.22H). GPC: $M_n = 3,374; M_w = 11,830$, PDI $=$ 3.51.

$P_{75T25}$ The same procedure used for $P_{95T5}$ was employed except the amounts of reagents used were as follows: 3 (70 mg, 0.05 mmol), Pt(PBu$_3$)$_2$Cl$_2$ (67 mg, 0.10 mmol), 1,4-bisethynylbenzene (18 mg, 0.15 mmol) and CuI (2 mg, 0.01 mmol). $P_{75T25}$ was obtained as a yellow solid (yield 85 mg, 78%). $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 0.81-1.04
(m, 72H), 1.32-1.74 (m, 96H), 1.85-2.24 (m, 48H), 6.58-6.02 (s, 1.53H), 7.04-7.15 (br, 7.22H), 7.18-7.29 (m, 4.96H). GPC: \(M_n = 28,873; M_w = 105,885; PDI = 3.67\).

\(P_{0T100}\) The same procedure used for \(P_{95T5}\) was employed except the amounts of reagents used were as follows: 2 (69 mg, 0.25 mmol), Pt(PBu3)2Cl2 (166.67mg, 0.25 mmol), tetrabutylammonium fluoride (1 M solution in THF 0.51 mL) and CuI (1 mg, 0.005 mmol). \(P_{0T100}\) was obtained as a yellow solid (145 mg, 80%) \(^1\)H NMR (300 MHz, CDCl3) \(\delta\) 0.09 (m, 18 H), 1.50 (m, 27 H), 2.1 (br 12 H), 6.48 (s, 2H) GPC: \(M_n = 39,132; M_w = 81,187; PDI = 2.08\).

**Photophysical Methods**

UV-Visible absorption spectra were obtained in 1 cm quartz cuvettes using a Perkin-Elmer 100 Spectrophotometer. Corrected, steady-state photoluminescence spectra were recorded on a SPEX F-112 fluorescence spectrophotometer. Samples were contained in 1 cm x 1 cm quartz cuvettes, and the optical density was adjusted to approximately 0.1 at the excitation wavelength. All photophysical measurements were carried out in argon degassed tetrahydrofuran solutions except for those conducted at 78 K, which were carried out in argon saturated 2-methyltetrahydrofuran, or where otherwise noted. Emission quantum yields are reported relative to Ru(bpy)3 in water for which \(\Phi = 0.055^{130}\) and an appropriate correction was applied for the difference in refractive indices of actinometer and sample solvent.\(^{108}\) Fluorescence quenching was carried out by performing a micro-scale titration in a fluorescence cuvette.

Time resolved emission and transient absorption experiments were performed by using the third harmonic of a Nd:YAG laser (355 nm, 10 ns fwhm, 10 mJ pulse) as the
excitation source. Regression analysis of the rate data was performed using SigmaPlot graphing software using built-in functions.
CHAPTER 4
META LINKED PLATINUM CONTAINING POLY(PHENYLENE ETHYNYLENE)S

Introduction

Because many biopolymers, including DNA and proteins, may adopt a helical conformation in solution there has been a significant effort to develop synthetic materials that can mimic the folding and unfolding processes of natural materials. In some of the first work on conjugated helical systems, the Moore group synthesized a series of phenylene ethynylene oligomers that self assemble into a helix in a poor solvent. However, the utility of these materials may be somewhat limited because of their hydrophobicity. Addressing this problem, Tan and coworkers synthesized two meta linked PPE with ionic pendant groups, making the polymers highly water soluble. These materials indeed proved to be have many of the properties of DNA, including helical self-assembly and the ability to accept intercalators. In addition, one of the interesting properties noted in both reports is that when meta-linked phenylene ethynlenes coil into a helical shape, their photoluminescence properties cease to correspond to those of single-chain polymers and instead resemble polymer aggregates. This is evidenced by solvent dependant changes to the optical properties of the materials.

The ability of meta linked PPEs to fold and unfold is related to their ability to adopt different conformations by rotation about carbon-carbon triple bonds. A four ring segment of a meta-linked oligo(phenylene ethynylene) (OPE) may adopt two limiting conformations. These are illustrated in Figure 4-1. In 4-1A, the oligomer adopts a trans-like (transoid) conformation, while in 4-1B the conformation is cis-like (cisoid).
Extrapolating from these depictions, it is clear that a polymer that consists of mainly transoid linkages will be essentially a random coil-like material, whereas a polymer consisting primarily of cisoid linkages will collapse into a helical superstructure.

Figure 4-1. Transoid (A) and cisoid (B) conformations of a tetrameric meta linked OPE.

The work described in this chapter explores the effects of introducing platinum into the meta linkages of a \( m \)-PPE. The study aims to determine whether the conformational changes illustrated in Figure 4-1 can still take place when platinum is introduced. Additionally, the effects of binding to small molecules will be explored. Finally, because incorporation of platinum allows access to the triplet manifold of arylene ethynylenes, it was hoped that a level of control over the anticipated aggregation effects could be exerted in order to allow for the observation of triplet excimer emission.

In addition to polymers, small molecule model compounds were considered for comparative purposes. The polymers and model compounds under consideration in this study, and their abbreviated nomenclature, are depicted in Figures 4-2. The
The nomenclature adopted for these materials is that P or M represent a polymer or model, and O or W signify solubility in organic or water based solvents.

Figure 4-2. Polymers and models featured in this study.

**Results and Discussion**

**Synthesis and Characterization**

The polymers and model compounds were designed so that the organic-soluble materials feature ester linkages that can easily be hydrolyzed to give the water soluble materials. The monomeric base unit in P-O and M-O is compound 3, which was synthesized from 2,5 diiodophenol as depicted in Figure 4-3.
Reagents and conditions: a) 2-bromoacetic acid, Na₂CO₃, DMF, reflux 16 hrs. (b) 1. Na₂CO₃, Water. 2. 1-bromododecane, DMF, reflux. (c) 1. Trimethylsilylacetylene, Pd(PPh₃)₄, Cul, THF, TEA, RT, 3 hrs. 2. TBAF, dioxane/acetic acid, RT 15 min.

Figure 4-3. Synthesis of monomer 3.

The first step of this synthesis involves substitution of bromine on 2-bromoacetic acid. Care must be taken to exclude air from this reaction to prevent oxidation of the phenol. Purification of the intermediate acid 1, is accomplished by dissolving the crude material in a minimal amount of aqueous sodium hydroxide and treating the solution with activated carbon. After removal of the charcoal, the pure product is recovered by adding hydrochloric acid to induce precipitation of the desired material as a pure, white solid.

Esterification of 1 can be accomplished by heating in dodecanol with catalytic acid and a Dean-Starke trap. However, this method proved inefficient, giving low quality, highly colored material and only moderate yields. It is likely that either 1 or its dodecyl ester decompose at the high temperatures (>150°C) required for that reaction. To circumvent this problem, the carboxylate salt was prepared by dissolving 1 in a small amount of water with a slight excess of sodium bicarbonate. After removal of the water by rotary evaporation, the recovered sodium carboxylate was allowed to react with 1-bromododecane in refluxing DMF. The reaction proceeds remarkably cleanly, with no apparent impurities by TLC analysis. The resulting ester is particularly susceptible to hydrolysis, an issue that must be taken into account in the remaining synthetic steps.
The final steps in the monomer synthesis are a Sonogashira coupling of 2 with trimethylsilylacetylyne followed by deprotection with tetrabutylammonium fluoride. This Sonogashira reaction is run with triethylamine instead of the more common diisopropylamine in order to prevent aminolysis of the ester. Amine catalyzed ester hydrolysis is a serious issue with this reaction unless strictly anhydrous conditions are enforced. Therefore the amine is mixed with THF prior to the reaction, and the mixture is freshly distilled from sodium hydride immediately before use. During the deprotection step this issue is addressed by adding a drop of acetic acid to the reaction mixture. The acid serves to immediately protonate the acetylide anions that are created when fluoride acts on the trimethylsilyl protecting group, preventing the establishment of a basic environment conducive to ester hydrolysis.

Trimethylphosphine was chosen as the ligand for platinum for this system for a variety of reasons. First, it is small compared to the tributylphosphine used with the polymers described in Chapter 3. This is important because a sterically bulky ligand would be anticipated to interfere with helix formation in the polymers. Additionally, because a hydrophilic polymer was a major part of the objective of this study, using the smallest alkyl groups possible seemed desirable to minimize the hydrophobicity of the final product. Unlike the polymers in Chapter 3, which relied on alkylphosphine ligands to provide solubility, the monomers described in this chapter have pendant groups on the aryl rings that are sufficient to solublize the final polymers.

The model compounds were synthesized as shown in Figure 4-4. Compound 3 was reacted with a mono substituted platinum chloride under Hagihara conditions in triethyl amine. As in the synthesis of the monomer, the solvent was distilled from sodium
hydride immediately before use to prevent premature hydrolysis. M-O is easily purified by column chromatography. Hydrolysis of M-O can be effected cleanly by sodium hydroxide in 2-methoxyethanol. The hydrolysis product, M-W, is recovered as a pure substance by precipitation in ether.

Figure 4-4. Synthesis of P-O. The specific conditions appear in the text and the experimental section.

Mass spectroscopy (MS) proved quite valuable in the characterization of M-W. The spectrum of the positive mode El MS appears in Figure 4-5. HRMS showed that M-W is isolated as a mixture of the protic acid and the sodium carboxylate salt. In fact, the MS matrix is sodiated upon incorporation of the M-W, as evidenced by a sodiated matrix peak at m/z = 571. Therefore, m/z peaks corresponding to fragments of both the acid and the sodium carboxylate appear, and as a further complication, many peaks appear as both [M+H] and as [M+Na]. Nevertheless, careful interpretation of the spectrum provides an excellent basis for characterizing the molecule. For example, the peaks centered at m/z = 1139 and 1117 correspond to the sodium carboxylate plus Na⁺ and H⁺, respectively, while the peak at m/z = 1094 corresponds to the protonated acid + H⁺. The large fragmentation peak at m/z = 1072 corresponds to the decarboxylated acid plus Na⁺ (or the decarboxylated sodium salt plus H⁺) while the peak at 1043 corresponds to the fragment resulting from loss of the entire pendant group (-OCH₂COOH) + Na⁺. A final logical fragment appears at m/z = 602. This fragment corresponds to a molecule that has
undergone decarboxylation and cleavage of one of the aryl-ethynyl bonds. (see Figure 4-5). In addition, a very small peak corresponding to trace amounts of potassium carboxylate was also found. All of these assignments are confirmed by high resolution mass spectrometry (HRMS), where their isotopic distributions match the expected results for the assigned fragments. M-W was also characterized by $^1$H NMR, and this data appears in the experimental section of this chapter.

The polymerization to produce P-O was performed by a Hagihara coupling reaction using bis(trimethylphosphine)platinum (II) chloride. Again, in order to prevent unwanted hydrolysis or aminolysis, the solvent, a mixture of dichloromethane and triethyl amine, was freshly distilled from sodium hydride immediately before use. The polymer was purified by repeated precipitation in methanol. Post-polymerization functionalization of P-O afforded P-W. The labile ester groups proved a significant advantage, as hydrolysis was affected by subjecting the polymer to a solution of tetrabutyl ammonium hydroxide in a dioxane-water mixture overnight at room temperature. The resulting polymer was purified by dialysis against millipure water for 36 hours. It was stored in an aqueous buffer solution of pH 6.5 to prevent irreversible aggregation.
Solvent Induced Conformational Effects

The folding and unfolding of the polymers used in this study is observable by photophysical methods. Specifically, UV/Visible absorption and photoluminescence spectroscopy are useful tools in monitoring this process. Thus, the absorption and photoluminescence spectra of P-O were recorded in mixtures of dichoromethane, a good solvent for the polymer, and hexanes, a poor solvent.

It is useful to precede discussion of the polymers under investigation here with a brief account of some previous work. Moore’s group made m-OPEs which showed two bands in their absorption spectra. One band was assigned to the polymer’s helical form and the other to the random-coil form. In that work, changing from a good solvent to a poor solvent caused an increase of the oscillator strength of the band associated with the helical conformation, and a concomitant decrease in oscillator strength of the band.
associated with the random coil conformation. It was also observed that the photoluminescence spectra of these polymers showed less “single chain” type emission and more excimer or aggregate-like emission as the amount of poor solvent increased. Analogous results were also observed in similar systems in the Schanze and Tew groups.49,51

The absorption and photoluminescence results for P-O are shown in Figure 4-6. In pure DCM, the P-O shows a strong band with $\lambda_{\text{max}} = 345$ nm with a high-energy (blue) shoulder at 327 nm. As the amount of hexanes increases, the oscillator strength of both bands decreases, and the absorption spectra blue-shift.

Figure 4-6. UV-Vis absorption (left) and photoluminescence (right) spectra of P-O in argon degassed mixtures of DCM and Hex. Solid line – 100% DCM; dotted line – 75% DCM, 25% Hex; dash-dot line – 50% DCM, 50% Hex; dashed line – 25% DCM, 75% Hex.

The photoluminescence spectra also show pronounced changes as the solvent varies. In pure DCM, P-O exhibits two emission bands. The lower energy band is centered at 550 nm. This band is strongly quenched by oxygen, and has a lifetime of 19 µs. On this basis, it is assigned as phosphorescence. The other emission band centered at 400 nm corresponds to fluorescence. As the amount of hexanes in the solvent mixture
increases, the fluorescence band decreases dramatically in intensity. However, only a slight red-shift is observed, and the fluorescence remains relatively narrow, even when hexanes is the dominant component of the solvent. This is unlike the situation in either Moore or Schanze’s materials, which featured dramatic spectral broadening and redshifts in the fluorescence with increasing fraction of poor solvent. Similar changes are observed in the phosphorescence (550 nm) band. As the amount of hexanes in the solvent increases, the intensity, quantum yield, and lifetime of the phosphorescence band all decrease. However, there is no concomitant change in the shape or wavelength of the phosphorescence band.

The results from the absorption spectra are somewhat ambiguous because the size of the spectral changes associated with variations in solvent composition is small. However, the changes in phosphorescence are consistent with those resulting from aggregation of linear platinum acetylide polymers. On this basis, the observed spectral changes are assigned to be the result of an aggregation effect. Based on previous work with meta-linked OPEs and PPEs, it is reasonable to presume that these results are not due to interchain aggregates, but instead intrachain aggregates caused by the polymer adopting a helical conformation which brings the phenylene rings in close proximity to one another. If this is so, then the polymer adopts its maximum extended conformation in pure DCM, and its most helical conformation in a mixture of 25% DCM and 75% hexanes. Note that the polymer is insoluble in higher volume fractions of hexanes. Also, it is impossible to determine from this information what fraction of the polymer is in a helical domain and what fraction is in a random coil domain in any particular composition of the solvent.
Similar results are observed for P-W. Absorption spectra of this polymer appear in Figure 4-7. In this experiment, the solvent composition was varied between methanol and water. Here, the highest oscillator strength is observed when the solvent is an 80:20 mixture of methanol and water. In this solvent mixture, the absorbance maximum is 325 nm, and there is a blue shoulder at 312 nm. As the amount of water in the solvent increases, the oscillator strength of both bands decreases and the spectrum undergoes a modest blue-shift. Additionally, the 312 nm shoulder increases in intensity as the amount of water increases. For example, in 80:20 methanol:water, the shoulder’s intensity is about 75% of that of the main band, while in 20:80 methanol:water, the shoulder and main band are of nearly equal intensity.

Figure 4-7. Absorbance spectra of P-W in mixtures of methanol and water.

In 100% water, the absorption of P-W in water is dependant on pH, as illustrated in Figure 4-8. The spectra in water all closely resemble that of the polymer in a mixture of 20% water and 80% methanol (Figure 4-7) in terms of their shape and absorption
maxima, which agrees with expectation if the polymer is mostly helical in this solvent. The absorption does not change significantly when pH > 7. This reflects that the acid side-groups are deprotonated under these conditions. As the solvent media becomes more acidic, the intensity of the absorption decreases. This change relates to conformation changes induced by protonation of the acid pendant groups.

Figure 4-8. Variable pH absorption spectra of P-W.

These results show that in water the polymer adopts a more helical conformation at high pH, when the acid pendant groups are protonated. This is logical, because when the side groups are deprotonated, columbic repulsion between the carboxylate anions should tend to force the polymer to adopt a more extended conformation. Conversely, protonated acid side groups tend to aggregate to maximize favorable hydrogen bonding interactions, which would favor a more helical conformation. Considering all of the solvent effects, P-W adopts a maximum extended conformation in a mixture of 80% methanol and 20% water, and its helicity is maximized in water at low pH.
Figure 4-9 shows photoluminescence spectra of P-W. The polymer is not phosphorescent, but it does exhibit a fluorescence band centered about 415 nm, the exact maximum being somewhat dependant on solvent composition. The most intense fluorescence is observed when the solvent mixture is 80% methanol and 20% water. This is consistent with the notion that the polymer adopts its most extended conformation in this solvent mixture. P-W is not emissive in water, regardless of pH. This supports the notion that the polymer is in a mostly helical conformation in water.

Notably, none of these effects appear when the model compounds M-O and M-W are treated under the same conditions. The models are non-emissive, and their absorption spectra do not show a significant dependence on solvent composition. This observation lends support to the idea that these spectral changes are truly the result of solvent induced conformation effects, and not simple interchain aggregation.
Chiral Induction

Many natural biological polymers, including nucleic acids and proteins are optically active and adopt only one of two possible helical enantiomers. Many examples exist where chirality is induced into an achiral synthetic polymer by taking advantage of interactions with chiral guest molecules.\textsuperscript{135-138} A variety of binding interactions including host-guest,\textsuperscript{135} acid-base,\textsuperscript{136} hydrogen-bonding,\textsuperscript{138} and electrostatics\textsuperscript{137} may be taken advantage of for this purpose. In two separate studies, the Moore\textsuperscript{132} and Schanze\textsuperscript{49,75} groups used (-)-\(\alpha\) pinene as a chiral guest to induce chirality in helical conjugated oligomers and polymers. In these studies circular dichroism (CD) spectroscopy was used to detect the interaction between the chiral guest and the host molecule. Addition of the chiral guest to the helical form of a conjugated material results in a significant CD Cotton effect. This indicates that there is preferential binding of the guest to one enantiomeric form of the helix.

Figure 4-10 shows the CD spectra of P-W in a solution composed of 60% water and 40% acetonitrile with increasing (-)-\(\alpha\) pinene concentration. Note that the polymer is expected to be in a primarily helical conformation in this solvent mixture. In the absence of (-)-\(\alpha\) pinene, the achiral polymer gives no CD signal. As the amount of (-)-\(\alpha\) pinene is increased, an induced CD signal is observed, and the strength of the signal increases with increasing concentration of (-)-\(\alpha\) pinene.

There are several features of the spectra in Figure 4-10 that are worth addressing. First, the CD signal does not appear in the characteristic “bis-signet” shape as observed in other studies with similar materials and in DNA.\textsuperscript{132} This may be because the transition moment for this Pt-containing PAE is not expected to be the same as in either DNA or the analogous all-organic m-PAE’s. There are examples of other chiral helical materials
that give a similar signal with one-sign only. The chromophore in this case is likely to have a transition dipole moment that is more alike to that of P-W than to DNA.

Figure 4-10. CD spectra of P-W in 60% methanol 40% acetonitrile with varying concentrations of (-)-\(\alpha\) pinene. The concentration of (-)-\(\alpha\) pinene varies from 0 to 6 mM, and the spectra were obtained 24 hours after addition of pinene.

Additionally, note that the optical density of the polymer solutions used in these experiments were approximately 0.8. Thus, the large CD signal implies that nearly all of the polymer chains in the sample adopt one helical enantiomer preferentially to the other. One possible explanation for this is that the difference in binding constants for the two enantiomeric helices to (-)-\(\alpha\) pinene may be very large. If this is so, a solution of P-W and (-)-\(\alpha\) pinene at equilibrium will have a large excess of one helical enantiomer.

Watanabe and coworkers demonstrated that helix folding and unfolding in polymers like P-W is often a slow process. In order to test this idea, CD spectra of polymer samples were taken ten minutes and twenty four hours after addition of (-)-\(\alpha\)
pinene to a polymer sample. The results, which appear in Figure 4-11 show that the intensity of the CD signal is more than 10 times greater when 24 hours has elapsed as compared to the intensity 10 minutes after adding the guest. Additional waiting did not result in any further increase in the CD signal, indicating that the system has completely equilibrated after 24 hours.

![CD spectra of P-W in 60% methanol 40% water with 6 mM added (-)-α pinene. Spectra were obtained 10 minutes and 24 hours after addition of (-)-α pinene.](image)

**Intercalator Binding**

The CD results clearly show that the polymer adopts a helical conformation in poor solvents such as water. Small aromatic and heteroaromatic chromophores are known to intercalate into the helical superstructure of DNA. Figure 4-12 is a depiction P-W in its helical conformation. Careful consideration of the structure of DNA and that of P-W reveals several interesting similarities. Both form helices that include face-to-face π staking of aromatic rings, and both have pendant anionic groups. Because of these
similarities, it was anticipated that DNA intercalators might also bind to P-W. The fact that Tan et. al. have previously shown that binding of DNA intercalators to an organic conjugated polyelectrolyte is possible in a previous study made this line of investigation seem particularly promising.\textsuperscript{49}

Figure 4-12. A twelve monomer segment of P-W in a helical conformation. Hydrogen atoms and some pendant P-alkyl groups have been omitted for clarity.

\[ \text{Ru(bpy)}_2(\text{dppz})^{2+}, \text{ where bpy = 2,2'-bipyridine and dppz = dipyrido[3,2-a:2’3’-c]phenazine (Rudppz) and 9-aminoacridine hydrochloride (AA) were used in this study.} \]

The structures of these materials appear in Figure 4-12. Rudppz has been extensively used as a DNA probe because its photoluminescence is negligible in water due to quenching associated with hydrogen bonding of water to the phenazine ligand. However, upon binding to DNA, the phenazine nitrogens are shielded from solvent interactions and strong photoluminescence results.\textsuperscript{140,141} This phenomenon is popularly referred to as the “light switch effect”.

\[ \text{Ru(bpy)}_2(\text{dppz})^{2+}, \text{ where bpy = 2,2'-bipyridine and dppz = dipyrido[3,2-a:2’3’-c]phenazine (Rudppz) and 9-aminoacridine hydrochloride (AA) were used in this study.} \]
It was initially anticipated that 9-anthrylmethylammonium chloride (AMA) would be used as an intercalator for this study. AMA is a well known DNA intercalator that exhibits significant changes in its absorption and photoluminescence characteristics upon binding to DNA. However, the absorption spectrum of AA overlaps with that of P-W, making it difficult to use optical spectroscopy to monitor its intercalation. AA was used instead because it is similar to AMA in both charge and structure, but features lower energy (red-shifted) absorption, which was expected to facilitate the use of spectroscopy to study this system.

The absorption of AA with added P-W is shown in Figure 4-13. In water (A), where the polymer adopts a primarily helical conformation, AA shows a hypochromic effect as the concentration of polymer increases. This effect saturates when the ratio of polymer repeat unit to AA is 10:1, and is similar to the effect observed when AMA is added to DNA. In a mixture of 80% methanol and 20% water (B), addition of the
polymer has no significant effect on the spectrum of AA.

Figure 4-14. Absorption spectrum of 10 µM AA with added P-W in (A) water (pH = 7, 0.5 mM tris buffer) and (B) methanol/water (80:20).

The triplet excited state of AA is accessible by laser excitation, and it can be monitored by laser flash photolysis. The effect of P-W on the AA triplet decay is shown in Figure 4-14. In the absence of polymer, the observed triplet lifetime of AA in water is 80 µs. In the presence of an excess of polymer (PRU:AA >10:1), the lifetime increases to 100 µs. This increase in lifetime represents a shielding of AA from the solvent, which can vibronically couple to the AA excited state thereby providing an additional non-radiative decay pathway. This is an expected result, and it conforms to the behavior of this type of system upon binding to DNA. As expected, addition of AA to the model compound M-W does not result in any spectral changes.
Figure 4-15. Decay of AA triplet absorption in free (dotted line) and intercalated (solid line) AA. The AA triplet-triplet absorption was monitored at 450 nm.

Intercalation of Rudppz is easily monitored by following its photoluminescence. Figure 4-15 shows that as a solution of Rudppz in water is titrated by P-W, its photoluminescence intensity increases. Figure 4-16 is a plot of the increase in photoluminescence intensity verses the ratio of polymer repeat units to Rudppz in both water and 80:20 methanol:water. This figure shows that the “light switch effect” is not observed when the solvent is an 80:20 mixture of methanol and water. Adding M-W to a Rudppz solution also fails to induce any fluorescence enhancement. In water, the photoluminescence turn-on effect saturates when the PRU:Ru ratio is 10:1. That the same ratio was found for Rudppz and AA indicates that the generalized PRU:intercalator binding ratio for this polymer is 10:1.
The 10:1 PRU:intercalator ratio is notable, because one turn of the polymer helix consists of only 6 PRU’s. Thus, the polymer binds less than one intercalator per turn. More insight into this is given in Figure 4-16. The plot in figure 4-16 which corresponds to the titration in water has two distinct regions. At low ratios of [PRU]:[Ru], the graph is linear, with a moderate slope. At higher ratios, the slope of the graph increases dramatically, until leveling off at 10:1 [PRU]:[Ru]. The inflection point occurs at 6:1 [PRU]:[Ru], corresponding to one binding site per turn of the helix. Thus, there are likely two modes of binding in this system. One mode likely corresponds to the situation when there is insufficient polymer to bind all of the intercalator. When the number of polymer turns is in excess of the amount of intercalator, a different binding mode is in effect.
Figure 4-17. Photoluminescence augmentation of Rudppz at 650 nm with addition of P-W in water (circles) and 80:20 methanol:water (triangles).

It is also notable that neither Rudppz nor AA show evidence of intercalation when the solvent is 80:20 methanol:water. This is a strong indication that in this solvent mixture the polymer adopts a completely random-coil conformation, with no helical domains. However, it is not possible to determine if the polymer’s conformation in water consists of completely helical domains or if it includes some random coil domains as well.

Conclusions

Two polymers, P-O and P-W, featuring meta linked Pt-acetylide backbones, were synthesized and characterized. Solvent dependant absorption and photoluminescence spectroscopy revealed that the polymers may adopt either a helical or random coil conformation, depending on the solvent composition.
Because of its helical shape and hydrophilicity, P-W is able to bind to small hetroaromatic molecules that are known to intercalate into helices of DNA, specifically Rudppz and AA. Because the spectral changes associated with binding of these molecules to P-W are identical to those associated with their intercalation into DNA, it is reasonable to conclude that AA and Rudppz bind to P-W by intercalation as well. The binding stoichiometry is greater than one intercalator per turn of the helix. That these effects are not observed when the model compound M-W is substituted for P-W confirms that the spectroscopic changes are the result of binding to the polymer helix and not a simple interaction with individual monomeric units.

Additionally, P-W exhibits strong induced chirality upon binding to the (-)-α pinene. This is evidenced by a strong induced CD signal of the bound polymer. Binding is a slow process, and the samples used in these experiments required at 24 hours to equilibrate and give the maximum possible induced CD signal.

**Experimental Section**

**Materials and General Synthesis**

THF was purchased from Acros and distilled over sodium/benzophenone prior to use. Tetrakis(triphenylphosphine)palladium was purchased from Strem and used as received. All other materials were purchased from either Acros or Aldrich and used as received except where noted. The synthesis of 4 and 3,5-diiodophenol have been described previously.\(^{44,144}\) Chromatography was carried out using silica gel (Merk, 230-400 mesh). NMR spectra were obtained on a Varian Gemini, VXR, or Mercury spectrometer operating at 300 MHZ, or an Inova spectrometer operating at 500 MHZ. GPC was preformed using a Rainin Dynamax model SD-200 solvent delivery system equipped with two PL-Gel 5 micron Mixed D columns (Polymer Laboratories, Inc.,
Amherst, MA) and a UV detector set at a wavelength where the polymer absorbs.

Molecular weight information was calculated from the chromatograms using Polymer Laboratories software.

**Synthetic Procedures**

**Compound 1.** To an erlenmeyer flask with a ground glass top and a magnetic stir bar was added sodium carbonate (7.6 g, 72 mmol), and α -bromoacetic acid (1.8 g, 13 mmol) and DMF (40 mL). A condenser was fitted to the top of the flask, and the system was heated gently to dissolve most of the sodium carbonate, and then sealed with a septum on top of the condenser and degassed by argon spurring for 20 minutes. 3,5 Diiodophenol (5 g, 15 mmol) was added quickly, and the solution was degassed by spurring for another 15 minutes. The solution was heated to a gentle reflux under a positive pressure of argon with strong stirring for 12 hours. After this time, the solution was cooled to room temperature and the remaining carbonate neutralized by careful addition of dilute hydrochloric acid. The resulting solution was then poured into 400 mL of water, and precipitation of the crude product was induced by dropwise addition of 6 N hydrochloric acid. The tan solid was collected by filtration, dried, and redissolved in a minimal amount of 1 N sodium hydroxide. This yellowish alkaline solution was treated with activated carbon and filtered. The clear supernatant was treated with dropwise addition of 6N hydrochloric acid to induce precipitation of the pure product as a white solid (yield, 2.45 g, 43 %). $^1$H NMR (DMSO, d$_6$) δ 7.53 (s, 1H), 7.25 (s, 2H), 4.78 (s, 2H). $^{13}$C NMR δ 170.4, 159.5, 137.8, 123.8, 96.7, 65.3.

**Compound 2.** To a 100 mL round bottom flask was added 1 (2 g, 5 mmol), sodium carbonate (600 mg, 612 mmol) and water (25 mL). The mixture was heated gently until the acid was completely dissolved. The water was then evaporated under
reduced pressure, and the residue was redissolved in DMF (40 mL). 1-Bromododecane (1.6 g, 6 mmol) was added and the solution was heated to reflux. The solution was maintained at reflux until TLC indicated that the acid was completely consumed (the acid remains on the baseline of our silica TLC plates when the eluent is 1:1 hexane to dichloromethane). The solution was then cooled to room temperature and poured into 300 mL of ice-water to induce precipitation of the product as an off-white solid. The product was collected by filtration, dried under high vacuum at 40°C to remove any remaining alkyl bromide, and recrystallized from methanol-water to give the desired product as a white solid (yield, 3.1 g, 91%). ¹H NMR (CDCl₃) δ 7.67 (s, 1 H), 7.24 (s, 2 H), 4.49 (s, 2 H), 4.21 (t, 2 H), 1.54 (br, 2 H), 1.21 (br, 18 H), 0.80 (t, 3 H).

**Compound 3.** To a freshly distilled, anhydrous solution of THF (10 mL) and diisopropylamine (5 mL) was added 2 (1.5 g, 2.6 mmol). The resulting solution was sealed with a septum and sparged with argon for twenty minutes. Excess trimethylsilyl acetylene (3 mL), and catalytic amounts of tetra(tributylphosphine) palladium (2 mg) and copper (I) iodide (2 mg) were added quickly. A voluminous white precipitate formed almost immediately. The solution was sparged with argon for another five minutes, and then kept under a positive pressure of argon. The reaction mixture was stirred at room temperature for three hours. During this time, the mixture turned black. After three hours, the reaction mixture was filtered, solids discarded, and the supernatant was removed by evaporation. The residue was then dissolved in hot hexanes (30 mL) and eluted through a short (approx. 7 cm x 3 cm) plug of silica with diethyl ether. The solvent was then removed, leaving a yellow oil. The oil was dissolved in dioxane (10 mL) and 1 mL of 50% aqueous acetic acid was added. This solution was sparged with argon for ten
minutes, and then a solution of tetrabutyl ammonium fluoride in THF (1 M, 5 mL), was added through the septum. The resulting solution was stirred at room temperature for fifteen minutes, and then poured into ice cold water to precipitate the crude product as an off white solid. The product required further purification by column chromatography with a mixture of hexanes and diethyl ether (15:1) as the eluent to give the pure product as a white solid (yield, 660 mg, 63%). $^1$H NMR (CDCl$_3$) $\delta$ 7.25 (s, 1 H) 7.05 (s, 2 H), 4.62 (s, 2 H), 4.20 (t, 3 H), 3.05 (s, 2 H), 1.63 (br, 2 H), 1.25 (br, 18 H), 0.84 (t, 3 H). $^{13}$C NMR $\delta$ 168.7, 158.6, 129.5, 123.8, 119.1, 82.5, 78.3, 65.9, 65.6, 32.1, 29.9, 29.9, 29.8, 29.7, 29.6, 29.5, 29.4, 28.7, 26.0, 22.9, 14.4. HRMS (EI, positive mode) calc. [M+H]$^+$ 368.2351, found [M+H]$^+$ 368.2351.

**P-O.** To a solution of dichloromethane and diisopropyl amine (2 mL, 3:1) that was freshly distilled over sodium hydride was added 3 (150 mg, 0.4 mmol) and bis(trimethylphosphine) platinum (II) chloride (170 mg, 0.4 mmol). The reaction mixture was spurged for 15 minutes with argon, and left under a positive pressure of argon while a catalytic amount (ca. 1 mg) of copper (I) iodide was added. The reaction mixture was heterogeneous at this point. After stirring at room temperature for thirty minutes, the reaction mixture became homogenous. The reaction was allowed to proceed for a total of five hours before it was quenched by precipitating the polymer in a large volume of methanol to which a few drops of acetic acid had been added. The product was recovered by filtration, redissolved in dichloromethane before it dried completely, and precipitated again in methanol with a few drops of acetic acid. The solid, pale yellow polymer was recovered by filtration (yield, 205 mg, 77%) GPC Mn = 9,400, Mw = 12,800 PDI = 1.36. $^1$H NMR (CDCl$_3$) $\delta$ 6.90 (s, 1 H), 6.83 (s, 2 H), 4.58 (s, 2 H), 4.11
(t, 2 H), 1.89 (br, 18 H), 1.22 (br, 18 H), 0.83 (t, 3 H). $^{13}$C NMR (CDCl$_3$) $\delta$ 169.2, 157.4, 128.8, 127.9, 65.7, 65.6, 32.1, 29.9, 29.8, 29.7, 29.6, 29.4, 28.7, 26.0, 22.9, 19.4, 16.3, 15.9, 15.7, 15.3, 14.4.

**P-W.** To 30 mL of dioxane was added P-O (150 mg). To this solution was added tetrabutylammonium hydroxide (3 mL, 1 M solution in methanol). The solution was stirred for thirty minutes, after which it became inhomogeneous. Water (2 mL) was added to redissolve the precipitate, and the solution was stirred overnight at room temperature. After this time, the solution was poured into 300 mL of cold diethyl ether and stirred vigorously. Methanol was added dropwise to induce precipitation of the polymer as a waxy, yellow solid. The solid polymer was collected by filtration and redissoled in 50 mL of millipure water in a dialysis bag (10 kD, cellulose). The polymer solution was dialyzed for thirty six hours against millipure water, and the water was changed every twelve hours during the dialysis. After dialysis, the pH of the solution was adjusted to approximately 6.5 by adding a few drops of a dilute aqueous sodium bicarbonate solution. The polymer solution was then filtered through a 0.45 µ filter, and stored in solution. The yield of the reaction was determined by diluting the final solution to a known volume, and determining the concentration of the solution by gravimetric analysis after drying aliquots of known volume (yield, 95 mg, 90 %).

**M-O.** A solution of THF and triethylamine (5 mL, 3:1) was freshly distilled from sodium hydride. To this solution was added 1 (30 mg, 0.083 mmol) and 3 (100 mg, 0.1 mmol). The resulting solution was sparged with argon for 20 minutes, and a catalytic amount of Cul (ca. 2 mg) was added. The solution was the sparged with argon for an additional 10 minutes. After this time, the solution became homogeneous and turned a
greenish color. The reaction was stirred at room temperature for 6 hours, after which time the solvent was removed by rotory-evaporation. Chromatography with hexanes:ethyl acetate (4:1) as the eluent afforded the pure product as a white solid (yield, 45 mg, 43%). $^1$H NMR (CDCl$_3$) $\delta$ 7.31 (d, 4 H), 7.22 (t, 4 H), 7.15 (d, 2 H), 6.97 (s, 1 H), 6.70 (s, 2 H), 4.55 (s, 2 H), 4.18 (t, 2 H), 1.67 (br, 36 H) 1.25 (br, 20 H) 0.08 (t, 3 H).

**M-W.** To a mixture of 2-methoxy methanol (3 mL) and two drops of millipure water was added M-O (45 mg, 0.035 mmol) and NaOH (4 mg, 0.1 mmol). The heterogeneous reaction mixture was stirred at room temperature under positive pressure of argon for 30 min. After this time, another 1 mg of NaOH was added, and the reaction was allowed to stir for an additional 30 min. The reaction mixture was homogeneous at this point. Diethyl ether (20 mL) was then added to induce precipitation of the product as a fine white powder. The mixture was cooled to 0$^\circ$C for three hours and the product was recovered as a fine white powder after centerfugation of the mixture and decanting the solvent (yield, 37 mg, 96%). $^1$H NMR (CD$_3$OD) $\delta$ 7.31 (m, 10 H), 6.82 (s, 1 H), 6.75 (s, 1 H), 4.30 (s, 2 H), 1.78 (t, 36 H). HRMS (EI, positive mode) calc. [M+H] 1117.2912, [M+H] 1117.2912.

**Photophysical Methods**

The water used in the experiments was prepared in a Millipure Milli-Q plus purification system and had a resistivity of not less than 18 M$\Omega$. Experiments in water were carried out in 0.5 mM tris(hydroxymethyl)aminomethane (tris) buffer adjusted to the specified pH by addition of appropriate amounts of acetic acid or sodium carbonate. When not specified the pH was 7. UV-Visible absorption spectra were obtained on a Varian Carey 100 spectrophotometer. Corrected steady-state emission spectra were
recorded on a SPEX F-112 fluorescence spectrophotometer. Samples were contained in
1 cm x 1 cm quartz cuvettes, and the optical density was adjusted to approximately 0.1 at
the excitation wavelength. Emission quantum yields are reported relative to Ru(bpy)$_3$ in
water for which $\Phi = 0.055^{130}$, and an appropriate correction was applied to account for
the differences in refractive indices of the actinometer and sample solvents.$^{131}$ Circular
dichroism (CD) experiments were obtained on an AVIV-202 circular dichroism
spectrometer. Samples were prepared in a 1:1 mixture of methanol and acetonitrile, and
the optical density of the polymer was adjusted to approximately 0.8 at its absorption
maximum. An appropriate amount of (-)-$\alpha$ pinene was added, and the solution was
stirred vigorously for 10 minutes and then allowed to sit for 24 hours before
measurements, except when otherwise noted.
CHAPTER 5
CONCLUSIONS

In the preceding chapters, the synthesis, characterization, and photophysical behavior of several PAEs was described. Organic and organometallic PAEs were studied, and the investigations included both linear rigid-rod materials and polymers that are able to vary their conformation in solution. Optical spectroscopy, including UV/Visible absorption, steady-state and time-resolved photoluminescence, and time-resolved transient absorption were used to probe the properties of these materials. Ultrafast pulse radiolysis at Brookhaven National Laboratory’s LEAF proved a useful supplement to these techniques.

Carrier Transport

Single chain poly(arylene ethynylene)s live up to their popular moniker “molecular wires”. These materials exhibit extraordinarily fast and efficient intrachain transport properties with respect to electrons (or holes), singlet and triplet excitons. This transport is largely due to the extensive orbital mixing between adjacent monomer units in PAEs. As a consequence, moieties designed to trap holes or excitons have a tendency to interact with the polymer main chain forming delocalized low energy regions instead of localized trap-sites.

In addition, the polydispersity inherent in PAEs further complicate attempts to measure carrier transport rates in these materials. Nonetheless, it was determined that the rate of hole transport in a single chain conjugated polymer is at least $1 \times 10^8$ s$^{-1}$. Triplet transport is much slower, occurring on timescales competitive with phosphorescence,
with rates of the order $10^6 \text{ s}^{-1}$. Importantly, even when the observable optical properties of a PAE are dominated by the triplet manifold, energy transfer in the singlet state is still an important process.

**Helical Self-Assembly**

Two meta-linked PAEs featuring platinum in their backbone were designed and synthesized. In good solvents, P-O and P-W exist as random coils, but in poor solvents they self-assemble into helices. The helical conformation is confirmed by using a chiral guest molecule to bind to P-W and induce preferential formation of one of two possible enantiomeric helices. Because it is hydrophilic, P-W has the ability to bind to small heteroaromatic molecules much in the same way that DNA does. Binding of AA and Rudppz only occurs in solvent systems where P-W adopts a helical conformation, and results in predictable spectral changes. Additionally, P-W can bind to the chiral guest molecule (-)-α pinene. This interaction results in P-W preferentially adopting one of the two possible enantiomeric helices, as evidenced by an induced CD signal.

**Future Outlook**

Conjugated polymers in general and PAEs in particular have a bright future as materials for a variety of applications. Many of the fundamental properties of these materials have been reported in this dissertation. However, there is still work to be accomplished if scientists are to gain a more complete understanding of these systems.

For example, direct observation of hole transport in PAEs is still impossible because the rate of hole injection in invariably slower than the rate of hole migration. This points to the need for new methods of charge injection that are significantly faster than those currently available.
With regards to triplet transport, it is impossible to directly attribute the rate constants determined experimentally to the carrier migration rates. Because the distribution of thiophene in the polymers is random, and the polymers are not monodisperse, the distance between the exciton and the trap is not identical for every exciton. The experiments therefore represent the average of several different distances of energy migration. One possible solution to this problem might be the synthesis of donor-bridge-acceptor type molecules where the donor’s triplet energy is higher than that of diethynylbenzene, the bridge is a phenylene-based Pt-acetylide, and the acceptor is thiophene or another moiety with a low-energy triplet state. If a series of these molecules with different bridge lengths were synthesized, time resolved emission experiments would likely yield definitive rate information.

Finally, the helical, Pt-acetylide polymer seems to be somewhat less ordered than corresponding all-organic analogues. This is likely due to steric effects related to the large trialkyl phosphine ligands on the metal. Development of a new ligand system that avoids the use of bulky groups might lead to materials with more ordered conformational transitions.
REFERENCES AND NOTES


Kamat, P.; Lieberman, M.; Lindsay, S.; Marcus, R. A.; Metzger, R. M.; Michel-
Beyerle, M. E.; Miller, J. R.; Newton, M. D.; Rilison, D. R.; Sankey, O.; Schanze,


65. Candeias, L. P.; Grozema, F. C.; Padmanaban, G.; Ramakrishnan, S.; Sibbeles, L.


A 1999, 103, 4341.


2000, 122, 8561.


As a point of reference, the calculations predict that the diphenylacetylene cation radical (n = 1) will exhibit two allowed transitions at $\lambda_{\text{max}} = 640$ and 406 nm. The computed absorption band maxima compare reasonably well with those determined experimentally ($\lambda_{\text{max}} = 805$ and 425 nm).


127. The error in these measurements is estimated to be +/- 10%.
BIOGRAPHICAL SKETCH

Eric Ely Silverman was born in Bronx, New York, and grew up in Thiells and Pomona, two small hamlets in New York’s lower Hudson River Valley. After graduation from North Rockland High School in 1996, Eric moved to Pittsburgh, Pennsylvania, where he received a Bachelor of Science in chemistry from Carnegie Mellon University in 2000. After receiving his undergraduate degree, he continued immediately on to graduate work at the University of Florida, where he began the pursuit a doctorate in chemistry. After graduation in May, 2005, Eric will begin his professional career as a Patent Examiner in the United States Patent and Trademark Office in Alexandria, Virginia.