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## Report Title

Final Report: New Polymeric Materials Incorporating Heteromatic Phosphabenzene Units

### ABSTRACT

The proposed project described the incorporation of aromatic phosphorus heterocycles into polymer main chains and side chains. While pyridine and thiazole have been explored extensively in polymer chemistry, the phosphorus analogs (phosphinine and thiaphosphole) have yet to be incorporated into macromolecular structures. Monomer syntheses were explored for both ring systems and polymerization efforts resulted in some success for phosphinine-containing oligomers. Synthetic method development for both phosphinine and thiaphosphole proved challenging, and a successful efficient route to polymerizable monomers has not yet been established. Further efforts have looked at other phosphorus containing monomers in conjugated structures.

This project has also been expanded to controlled polycondensation for semiconducting polymers. Furan, which is a biorenewable monomer, has been explored in controlled polycondensation. High molecular weights could not be achieved due to aggregation but the furan was incorporated into an alternating polymer with thiophene to obtain solution-processable materials.

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**Enter List of papers submitted or published that acknowledge ARO support from the start of the project to the date of this printing. List the papers, including journal references, in the following categories:**

**(a) Papers published in peer-reviewed journals (N/A for none)**

<u>Received</u>	<u>Paper</u>
09/28/2016	6 Joshua C. Worch, Erich Helleman, Gabrielle Pros, Chakicherla Gayathri, Tomislav Pintauer, Roberto R. Gil, Kevin J. T. Noonan. Stability and Reactivity of 1,3-Benzothiaphosphole: Metalation and Diels-Alder Chemistry, <i>Organometallics</i> , (07 2015): 5366. doi:
09/28/2016	8 Yunyan Qiu, Joshua C. Worch, Andria Fortney, Chakicherla Gayathri, Roberto R. Gil, Kevin J. T. Noonan. Nickel-Catalyzed Suzuki Polycondensation for Controlled Synthesis of Ester-Functionalized Conjugated Polymers, <i>Macromolecules</i> , ( ): 4757. doi:
09/28/2016	9 Chia-Hua Tsai, Andria Fortney, Yunyan Qiu, Roberto R. Gil, David Yaron, Tomasz Kowalewski, Kevin J. T. Noonan. Conjugated Polymers with Repeated Sequences of Group 16 Heterocycles Synthesized through Catalyst-Transfer Polycondensation, <i>Journal of the American Chemical Society</i> , ( ): 6798. doi:
09/28/2016	10 Yunyan Qiu, Andria Fortney, Chia-Hua Tsai, Matthew A. Baker, Roberto R. Gil, Tomasz Kowalewski, Kevin J. T. Noonan. Synthesis of Polyfuran and Thiophene-Furan Alternating Copolymers Using Catalyst-Transfer Polycondensation, <i>ACS Macro Letters</i> , ( ): 332. doi:
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<b>TOTAL:</b>	<b>5</b>

Number of Papers published in peer-reviewed journals:

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**(b) Papers published in non-peer-reviewed journals (N/A for none)**

Received      Paper

**TOTAL:**

Number of Papers published in non peer-reviewed journals:

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**(c) Presentations**

Number of Presentations: 0.00

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**Non Peer-Reviewed Conference Proceeding publications (other than abstracts):**

Received      Paper

**TOTAL:**

Number of Non Peer-Reviewed Conference Proceeding publications (other than abstracts):

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**Peer-Reviewed Conference Proceeding publications (other than abstracts):**

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Number of Peer-Reviewed Conference Proceeding publications (other than abstracts):

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**(d) Manuscripts**

Received      Paper

**TOTAL:**

Number of Manuscripts:

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**Books**

Received      Book

**TOTAL:**

Received      Book Chapter

**TOTAL:**

**Patents Submitted**

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**Patents Awarded**

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**Awards**

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**Graduate Students**

<u>NAME</u>	<u>PERCENT SUPPORTED</u>	Discipline
Joshua Worch	0.46	
<b>FTE Equivalent:</b>	<b>0.46</b>	
<b>Total Number:</b>	<b>1</b>	

**Names of Post Doctorates**

<u>NAME</u>	<u>PERCENT SUPPORTED</u>
<b>FTE Equivalent:</b>	
<b>Total Number:</b>	

**Names of Faculty Supported**

<u>NAME</u>	<u>PERCENT SUPPORTED</u>	National Academy Member
Kevin Noonan	0.02	
<b>FTE Equivalent:</b>	<b>0.02</b>	
<b>Total Number:</b>	<b>1</b>	

**Names of Under Graduate students supported**

<u>NAME</u>	<u>PERCENT SUPPORTED</u>
<b>FTE Equivalent:</b>	
<b>Total Number:</b>	

**Student Metrics**

This section only applies to graduating undergraduates supported by this agreement in this reporting period

The number of undergraduates funded by this agreement who graduated during this period: ..... 0.00

The number of undergraduates funded by this agreement who graduated during this period with a degree in science, mathematics, engineering, or technology fields:..... 0.00

The number of undergraduates funded by your agreement who graduated during this period and will continue to pursue a graduate or Ph.D. degree in science, mathematics, engineering, or technology fields:..... 0.00

Number of graduating undergraduates who achieved a 3.5 GPA to 4.0 (4.0 max scale):..... 0.00

Number of graduating undergraduates funded by a DoD funded Center of Excellence grant for Education, Research and Engineering:..... 0.00

The number of undergraduates funded by your agreement who graduated during this period and intend to work for the Department of Defense ..... 0.00

The number of undergraduates funded by your agreement who graduated during this period and will receive scholarships or fellowships for further studies in science, mathematics, engineering or technology fields:..... 0.00

**Names of Personnel receiving masters degrees**

<u>NAME</u>
<b>Total Number:</b>

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**Names of personnel receiving PhDs**

<u>NAME</u> Joshua Worch Yunyan Qiu <b>Total Number:</b>	   <b>2</b>
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**Names of other research staff**

<u>NAME</u>	<u>PERCENT SUPPORTED</u>
<b>FTE Equivalent:</b>	
<b>Total Number:</b>	

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**Sub Contractors (DD882)**

**Inventions (DD882)**

**Scientific Progress**

See Attachment

**Technology Transfer**

See Attachment

**New Polymeric Materials Incorporating Heteroaromatic Phosphabenzene Units**

Principal Investigator:	Kevin J. T. Noonan
Organization:	Carnegie Mellon University Department of Chemistry 4400 Fifth Ave 15213
Proposal Number:	63038CHYIP
Agreement Number:	W911NF1310214
Period Covered by Report:	Final (08/01/2015 – 06/30/2016)
Author of Report:	Kevin J. T. Noonan

## Papers Published in Peer-Reviewed Journals (4)

- 1 Qiu, Y.; Worch, J. W.; Fortney, A.; Gayathri, C.; Gil, R. R.; Noonan, K. J. T. Nickel-Catalyzed Suzuki Polycondensation for Controlled Synthesis of Ester-Functionalized Conjugated Polymers. *Macromolecules*. **2016**, *49*, 4757-4762.
- 2 Tsai, C.-H.; Fortney, A.; Qiu, Y.; Gil, R. R.; Yaron, D. Kowalewski, T.; Noonan, K. J. T. Conjugated Polymers with Repeated Sequences of Group 16 Heterocycles Synthesized through Catalyst-Transfer Polycondensation. *Journal of the American Chemical Society*, **2016**, *138*, 6798-6804.
- 3 Qiu, Y.; Fortney, A.; Tsai, C.-H.; Baker, M. A.; Kowalewski, T.; Noonan, K. J. T. Synthesis of Polyfuran and Thiophene-Furan Alternating Copolymers Using Catalyst-Transfer Polycondensation. *ACS Macro Letters* **2016**, *5*, 332-336.
- 4 Worch, J. C.; Helleman, E.; Pros, G.; Gayathri, C.; Pintauer, T.; Gil, R. R.; Noonan, K. J. T. Stability and Reactivity of 1,3-Benzothiaphosphole: Metalation and Diels-Alder Chemistry. *Organometallics* **2015**, *34*, 5366-5373.

## Presentations (4)

- 1 Presentation at national meeting. Abstract was published but no conference proceedings available. Fall ACS Conference in Philadelphia, PA, Invited Talk in Sequence-Controlled Polymers Symposium, POLY Division, August 21-25, 2016
- 2 Presentation at Gordon Research Conference. No conference proceedings available. Organometallic Chemistry at Salve Regina, Submitted Poster, July 10<sup>th</sup>-July 15<sup>th</sup>, 2016
- 3 Presentation at Canadian national meeting. Abstract was published but no conference proceedings available. Canadian Society of Chemistry Conference, Halifax, NS, Submitted Talk in the Functional Organic pi-Systems Symposium, Organic Chemistry Division, June 9<sup>th</sup>, 2016

- 4 Presentation at national meeting. Abstract was published but no conference proceedings available. ACS Conference in San Diego, CA, Invited Talk in Polymer Related Energy Conversion & Storage Symposium, March 15<sup>th</sup> 2016

#### Student Support (1)

Joshua Worch, 46% FTE (Josh was supported from mid August to December 2015 and mid May to mid June 2016).

#### Faculty Support (1)

Kevin Noonan, 2% FTE (1 week of summer salary)

### Proposal Abstract

The proposed project described the incorporation of aromatic phosphorus heterocycles into polymer main chains and side chains. While pyridine and thiazole have been explored extensively in polymer chemistry, the phosphorus analogs (phosphinine and thiaphosphole) have yet to be incorporated into macromolecular structures. Monomer syntheses were explored for both ring systems and polymerization efforts resulted in some success for phosphinine-containing oligomers. Synthetic method development for both phosphinine and thiaphosphole proved challenging, and a successful efficient route to polymerizable monomers has not yet been established. Further efforts have looked at other phosphorus containing monomers in conjugated structures.

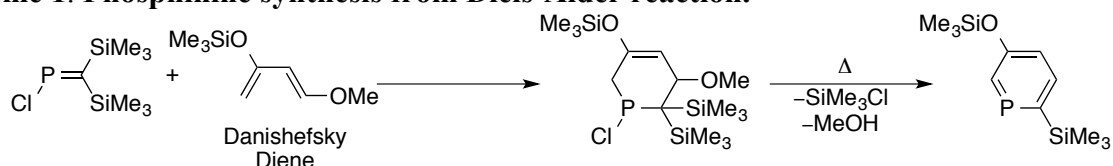
This project has also been expanded to controlled polycondensation for semiconducting polymers. Furan, which is a biorenewable monomer, has been explored in controlled polycondensation. High molecular weights could not be achieved due to aggregation but the furan was incorporated into an alternating polymer with thiophene to obtain solution-processable materials.

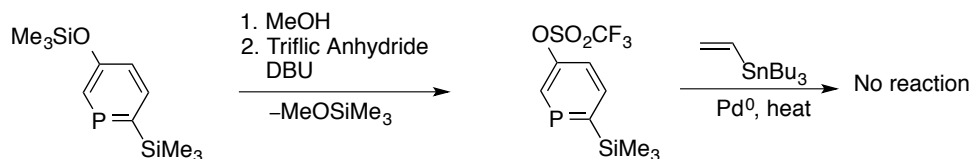
### Scientific Progress

#### Project 1 – Phosphabenzene Materials

In the proposal, we outlined unusual aromatic rings with phosphorus and the incorporation of these heterocycles into polymeric materials. We explored P=C bonds in Diels-Alder reactions to synthesize the desired phosphinine. We successfully obtained the 6-membered phosphorus heterocycle and converted it into a triflate (Scheme 1). We expected the triflate group to be active in palladium-catalyzed cross-coupling and we attempted a Stille reaction with tributyl(vinyl)tin and the triflyl-phosphinine. Unfortunately, the desired product could not be obtained regardless of the conditions attempted. We also attempted several other Diels-Alder strategies with limited success in forming the desired vinyl phosphinine for polymerization.<sup>1-2</sup>

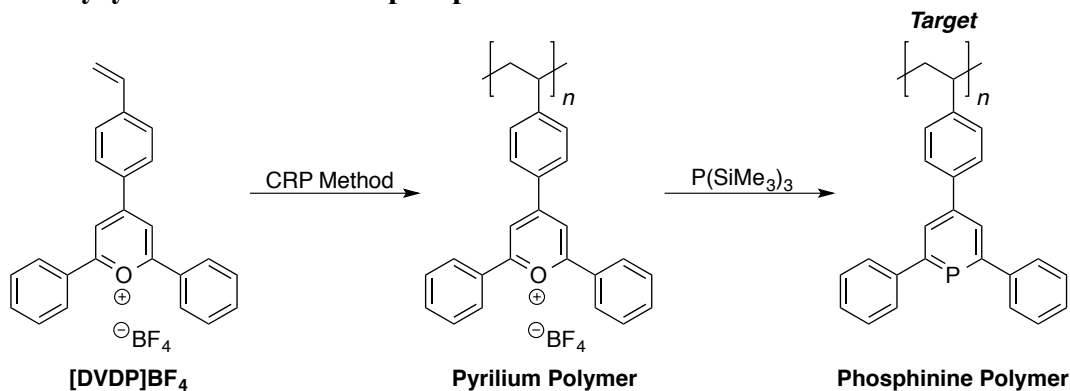
#### Scheme 1. Phosphinine synthesis from Diels-Alder reaction.



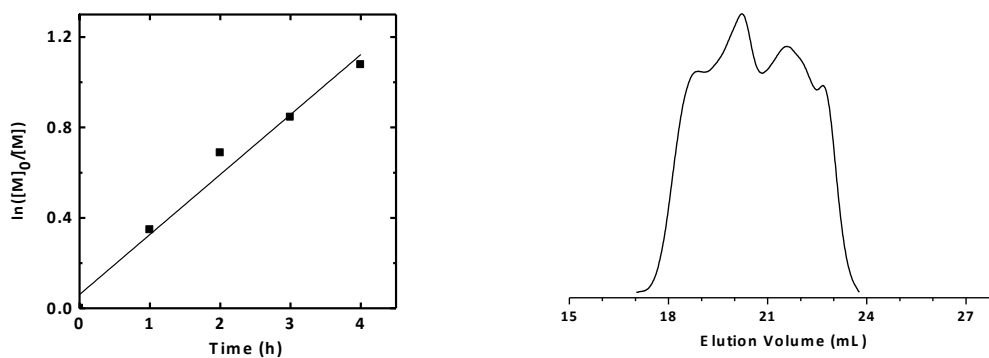


We also targeted pyrylium salts as precursors for phosphinine polymers. The **[DVDP]BF<sub>4</sub>** salt was synthesized (Scheme 2) and explored in a controlled radical polymerization process (Atom-transfer radical polymerization – ATRP). The resultant polymer could then be treated with P(SiMe<sub>3</sub>)<sub>3</sub> to afford the phosphinine polymer by nucleophilic substitution.

**Scheme 2. Pyrylium conversion to phosphinine.**



We discovered that consumption of the **[DVDP]BF<sub>4</sub>** monomer takes place using ATRP and the kinetics of the process are consistent with 1<sup>st</sup> order polymerization behavior (Figure 1). However, though the monomer was being consumed, a well-defined polymer was not obtained.



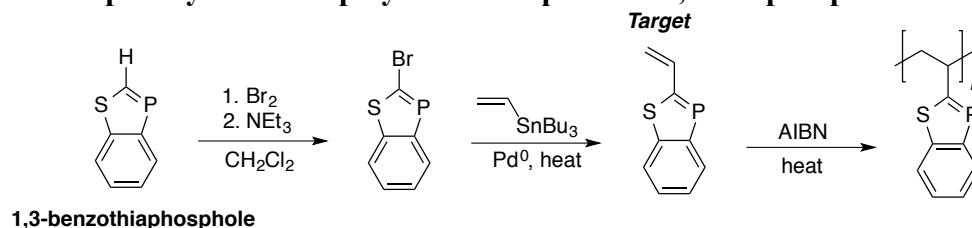
**Figure 1.** Left: Kinetic plot of ATRP of **[DVDP]BF<sub>4</sub>**. Right: GPC trace of poly**[DVDP]BF<sub>4</sub>** measured using DMF containing 10 mM NaBF<sub>4</sub> as the eluent.

The problem seems to be increasing the number of repeat units in the polymer chain. We suspect the bulky monomer allows for formation of small oligomers but then terminates as the steric congestion limits conversion to higher molecular weights. Altering conditions (solvents, temperature, initiator concentration) did not seem to result in the desired polymerization behavior. We could exchange the oxygen for phosphorus, to obtain phosphorus oligomers but, at this point, we turned our attention to the thiophosphole.

## Project 2 – Thiaphosphole Polymers

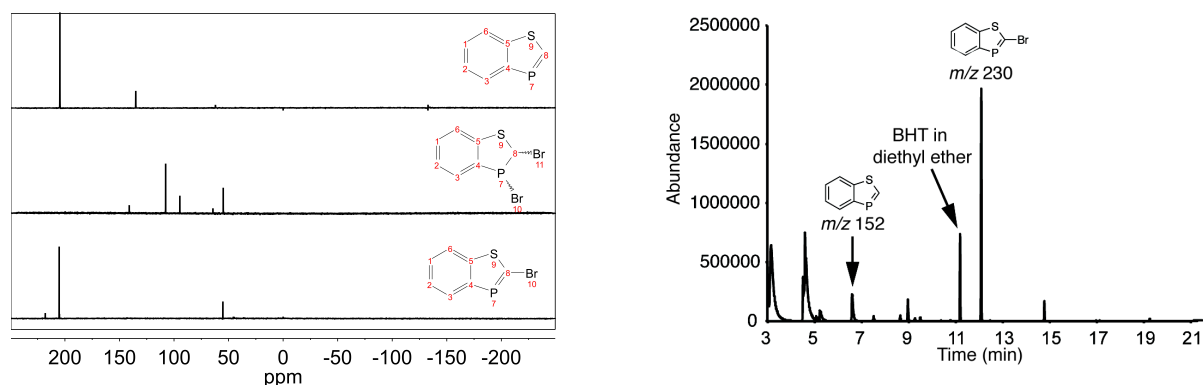
While exploring the phosphinine compounds, we began researching thiaphospholes and realized only a few reports existed for these molecules.<sup>3</sup> We started to explore these phosphorus rings as possible components in macromolecules. Prior to targeting polymer materials we explored model compounds to evaluate electronic and photophysical properties.<sup>4-5</sup> We then targeted a vinyl thiaphosphole, which could be explored in radical polymerization.

### Scheme 3. Attempted synthesis of polymers with pendant 1,3-thiaphospholes.



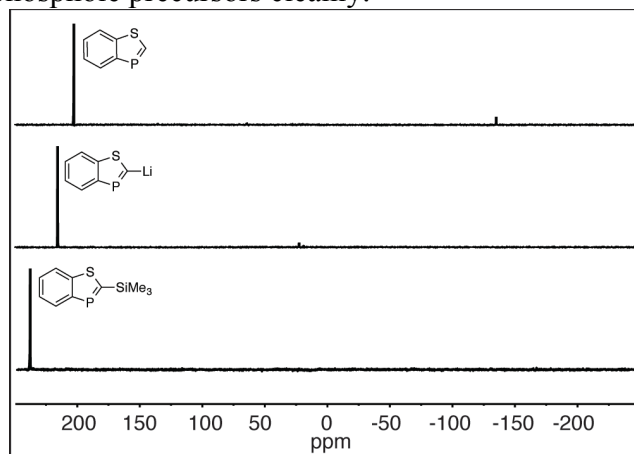
We synthesized the 1,3-benzothiaphosphole from 1-mercapto-2-phosphinobenzene and a formaldehyde equivalent. We confirmed the formation of the aromatic ring using  $^{31}\text{P}$  NMR ( $\delta = 203$  ppm) and  $^1\text{H}$  NMR spectroscopy. We noted the proton of the 2-position resonates significantly downfield at 8.86 ppm with a  $J_{\text{PH}}$  of 33.9 Hz. We could not isolate the parent thiaphosphole but we could manipulate it *in-situ* and we explored functionalization.<sup>6</sup>

When 1,3-benzothiaphosphole was treated with stoichiometric  $\text{Br}_2$  (Scheme 3),  $^{31}\text{P}$  spectroscopy indicated rapid attack at the  $\text{P}=\text{C}$  bond and new signals were observed ( $\delta^{31}\text{P}$  108,  $\delta^{31}\text{P}$  95,  $\delta^{31}\text{P}$  55). The signals at 108 and 95 ppm are postulated to be isomers of the 1,2-addition product while the signal at 55 ppm is unidentified. Addition of 1 equivalent of triethylamine, led once again to the formation of new signals ( $\delta^{31}\text{P}$  218,  $\delta^{31}\text{P}$  205), and we suspected the major signal at 205 ppm corresponded to the desired 2-bromo-1,3-thiaphosphole. Analysis of the reaction mixture using GC-MS (Figure 2) revealed a major product with molecular ion peak at 230 amu and the expected isotope pattern of a brominated molecule ( $M+2$  peak = 232 amu). After column chromatography under  $\text{N}_2$ ,  $^{31}\text{P}$  spectroscopy of the diluted product fraction revealed only one signal at  $\delta^{31}\text{P}$  205 which we anticipated was the product. However, upon concentration, the white crystalline solid became substantially discolored within minutes and a red residue formed. Analysis of the residue revealed complete degradation.



**Figure 2.** Left  $^{31}\text{P}$  NMR stack plot to illustrate formation of 2-bromo-1,3-benzothiaphosphole. Right – GC-MS of crude reaction mixture.

Since the 2-bromo-1,3-benzothiaphosphole was not isolable, we attempted an alternative strategy to make a functional thiaphosphole. We explored a lithiation and quenching strategy since the proton of the 2-position is relatively acidic. Using lithium diisopropyl amide (LDA) we were successfully able to lithiate the benzothiaphosphole at low temperature ( $\delta^{31}\text{P}$  216). The downfield shift in the spectrum indicated that the P=C bond remained intact during the reaction (Figure 3). The lithiated benzothiaphosphole reacted smoothly with  $\text{Me}_3\text{SiCl}$  and the 2-(trimethylsilyl)-1,3-benzothiaphosphole could be isolated in fairly low yield. We attempted some coupling reactions with this reagent but we could not successfully remove the trimethylsilyl group and install other functionality. We tried several other electrophiles but could not isolate any of the desired thiaphosphole precursors cleanly.

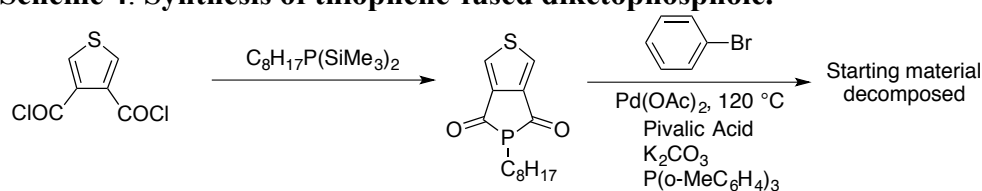


**Figure 3.** Stack Plot of the  $^{31}\text{P}$  NMR spectra for benzothiaphosphole lithiation and quenching using  $\text{Me}_3\text{SiCl}$ .

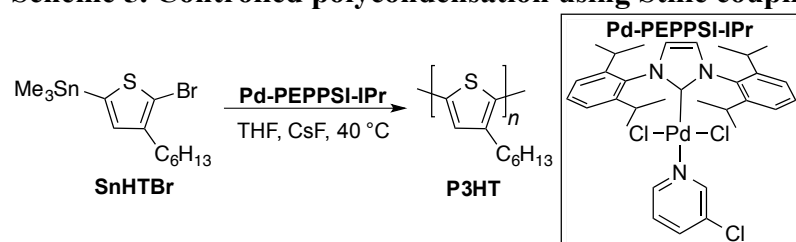
At this juncture, we decided to investigate some more common monomers in polycondensation reactions and we directed our efforts on phosphorus-based molecules away from P=C motifs as these seem to lack sufficient long-term stability for incorporation into polymers.

### Project 3 – Alternative Phosphorus Motifs in Conjugated Molecules

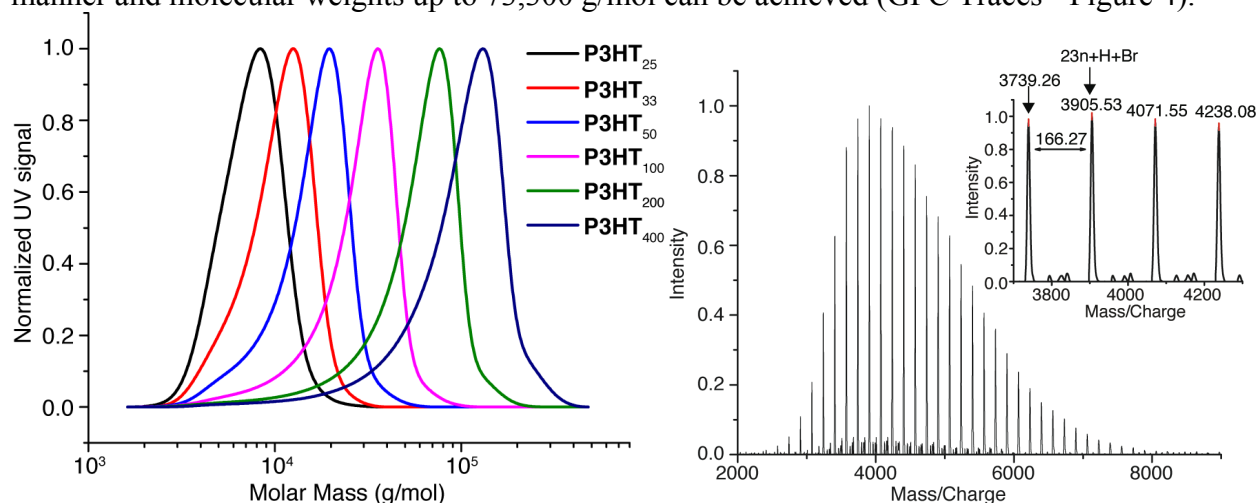
We began to explore other conjugated scaffolds bearing phosphorus, including the diketophospholes. These are similar to diimides, and they attracted our attention as potential electron-accepting building blocks. We successfully synthesized one of these molecules from a thiophene precursor (Scheme 4). Though the product was stable in air at room temperature, when we attempted to couple this to other aromatics directly using C-H activation protocols, the diketophosphole seemed to decompose. Its not clear if decomposition is due to the high temperatures employed in these reactions or if the palladium is involved in some sort of ring-opening process. While we were investigating these species, a report appeared in *Chemistry-A European Journal*.<sup>7</sup> The report described a series of polymers bearing this motif, which was very exciting, and the unit is indeed a very interesting electron-poor building block. One noteworthy aspect for our synthesis is the incorporation of alkyl substituents on the P atom. These can act as solubilizing groups for conjugated molecules and the prior report only described phenyl-substituted variants. We intend to publish a complementary manuscript illustrating how to form alkyl-substituted derivatives in the future and not only for these phosphorus containing motifs but for a variety of others as well. We envision this as another way to manipulate the electronic properties of these materials and improve or alter solubility.

**Scheme 4. Synthesis of thiophene-fused diketophosphole.****Project 4 – Catalyst-Transfer Polycondensation using Stille Coupling**

While working on the thiophospholes, we began to revisit some of the chemistry of thiophenes. We noted that one of the large limitations in controlled polymerization of thiophenes was the lack of functional group tolerance; the side-chains are limited because highly nucleophilic Grignard reagents are often employed as monomers.<sup>8-9</sup> To combat this, we began to explore Stille coupling chemistry as a means to controlled polythiophenes. Stille coupling has excellent functional group tolerance and should be amenable to a large number of aromatic rings and side-chains.

**Scheme 5. Controlled polycondensation using Stille coupling.**

We synthesized the prerequisite A-B monomer (**SnHTBr**) and began exploring catalysts for polymerization (Scheme 5). We investigated Pd-PEPPSI-IPr since electron-rich ligands such as the N-heterocyclic carbene often perform well in chain-growth polymerization of conjugated monomers. We discovered that the polymerization of **SnHTBr** proceeds in a well-controlled manner and molecular weights up to 73,300 g/mol can be achieved (GPC Traces - Figure 4).<sup>10</sup>



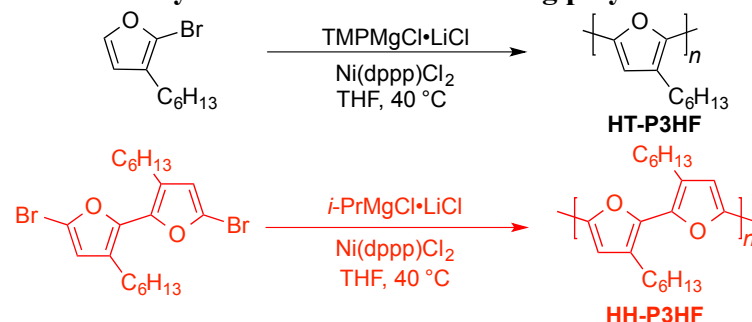
**Figure 4.** Left GPC traces of polymer samples obtained by altering catalyst loading. Right – MALDI-TOF of a polymerization reaction illustrating H/Br end-groups.

We noted a small increase in dispersity as higher molecular weights were targeted (up to 1.53) which is likely due to some termination as the reaction time increases. We obtained a monomer versus conversion plot to ensure the reaction was a chain-growth process and we conducted MALDI-TOF experiments to look at the end-group distribution in the polymer (Figure 4). Overall, the reaction proceeds in a chain-growth manner with controllable molecular weights, modest dispersities and good end-group fidelity. We have started to investigate other potential monomers using this protocol and we have also started to explore other catalysts for this reaction.

### Project 5 –Polyfuran: Semiconducting Materials From Biorenewable Monomers

After our investigation of polythiophene, we turned our attention to an overlooked monomer in the Group 16 heterocycles, furan. Furan is very electron-rich and suffers from some stability problems as it is not quite as aromatic as thiophene and selenophene. However, it can be obtained from sugars, and is a highly attractive monomer for semiconducting materials.

#### Scheme 6. Synthesis of furan-containing polymers

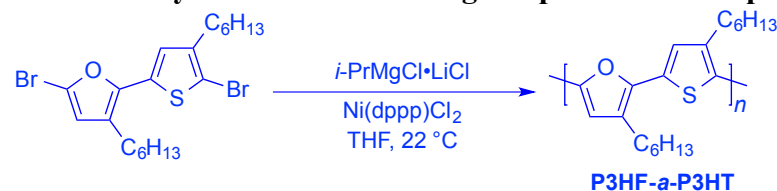


We synthesized two monomers to obtain different side-chain orientations and then began to investigate Kumada catalyst transfer polycondensation of these compounds (Scheme 5). We discovered two interesting features of the reaction.

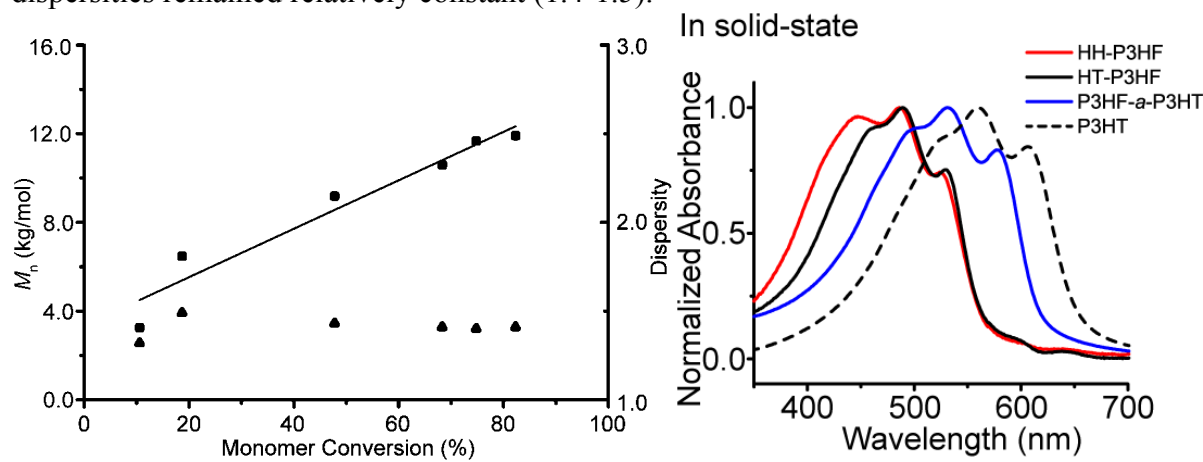
- 1) The polymerization of both monomers proceeds to relatively low molecular weights ( $M_n \sim 4000$ ,  $D \sim 1.2$ ). This is a result of extensive aggregation during the polymerization. However, the low dispersities are indicative of a chain-growth reaction.
- 2) The polymers adopt identical conformations in the solid-state as determined by UV-Vis spectroscopy, regardless of the side-chain pattern. The small atomic size of oxygen minimizes steric strain of the solubilizing groups making it highly attractive for conjugated architectures. (Figure 5 - Right)

To determine whether furan is amenable to chain-growth reactions, an alternating copolymer of thiophene and furan was envisioned. This structure would lower the furan content along the polymer chain and provide a certain amount of torsion along the backbone to improve solubility. The thiophene-furan dimer was synthesized, activated using  $i\text{-PrMgCl} \cdot LiCl$  and polymerized in THF. A range of molecular weights for the **P3HF-*a*-P3HT** could be achieved.

#### Scheme 7. Synthesis of alternating thiophene-furan copolymer.



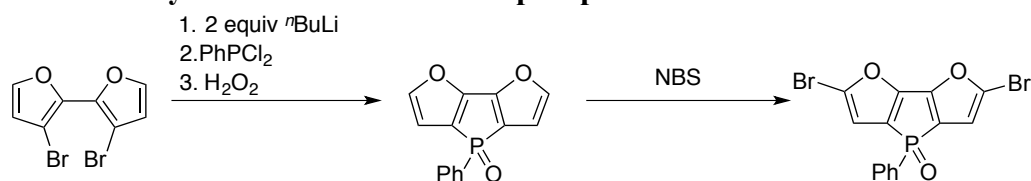
The alternating polymer was synthesized using 1.25 mol % of Ni(dppp)Cl<sub>2</sub> and aliquots were removed periodically and analyzed using GC-MS and GPC (Figure 5). A linear relationship between  $M_n$  and monomer conversion was observed, indicating a controlled process and the dispersities remained relatively constant (1.4-1.5).



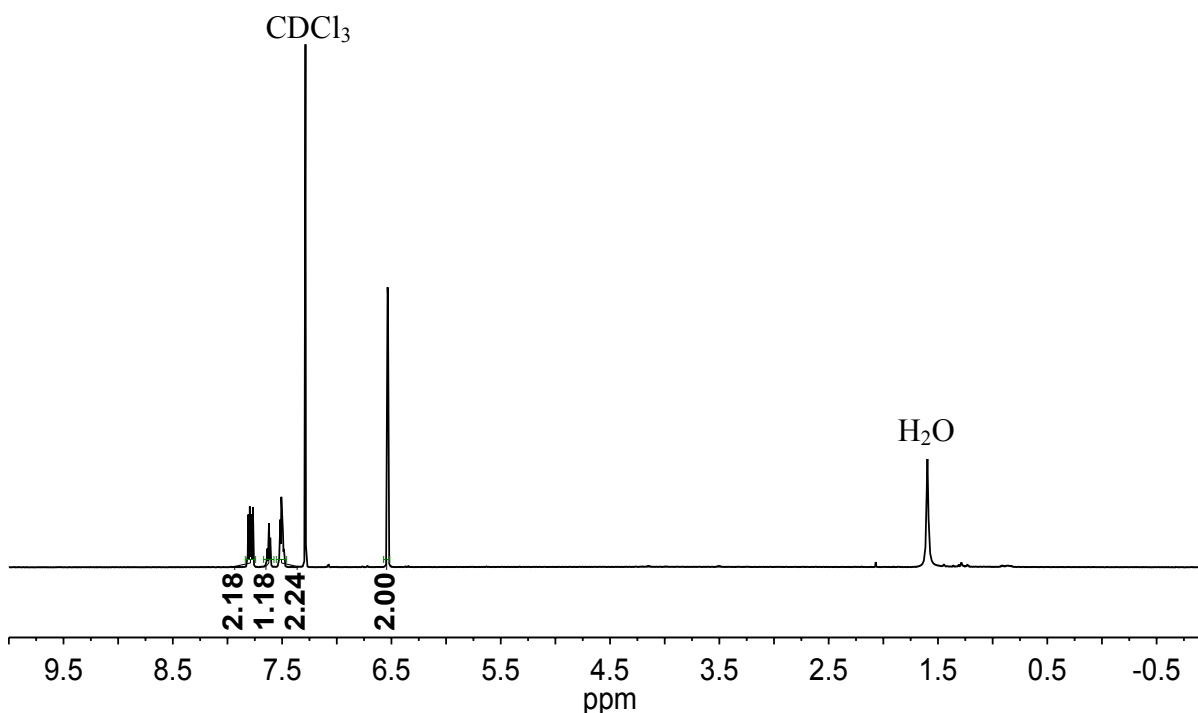
**Figure 5.** Left - Plot of  $M_n$  versus conversion for polymerization of **P3HF-a-P3HT** using 1.25 mol % Ni(dppp)Cl<sub>2</sub>. Right – UV Vis spectroscopy of **HT-P3HF**, **HH-P3HF**, **P3HF-a-P3HT** compared to poly(3-hexylthiophene) (P3HT).

We have started to combine our interest in furan with our interest in phosphorus-based conjugated architectures. We have noted that alkylated furans suffer from some stability issues in the presence of O<sub>2</sub> and light, which can be attributed to a Diels-Alder reaction. In an effort to stabilize this aromatic ring-system, one can append electron-withdrawing groups to the conjugated structure to manipulate the electronic properties of the system. A phosphine oxide seemed ideal for this purpose since it is strongly withdrawing.

#### Scheme 8. Synthesis of difuran-fused phosphole.



We synthesized a difuran-fused phosphole by preparing a 3,3'-dibromo-2,2'-bifuran, lithiating using butyllithium, and quenching using phenyldichlorophosphine (Scheme 8). Oxidation using hydrogen peroxide furnished the phosphole oxide, which could be brominated using N-bromosuccinimide (<sup>1</sup>H NMR Spectrum, Figure 6). We have noted these structures are stable under air and we are currently exploring Suzuki and Stille cross-coupling methods to polymerize this monomer. We have also synthesized a difuran-fused silole to make some direct comparisons between the phosphoryl and silyl moieties.



**Figure 6.**  $^1\text{H}$  NMR Spectrum of brominated difuran-fused phosphole.

### Future Directions

We are currently expanding our investigation of controlled polycondensation for semiconducting polymer materials and in particular, we are interested in sequence control within semiconducting polymers. These items have been discussed in more depth in our interim progress report for (68385-CH). We intend to complete the projects on the conjugated phosphorus ring-systems in the future.

### References

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