Functionalized polystyrene resin for isolating conjugated polymers with precise sequences

Thesis by

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In Partial Fulfillment of the Requirements

For the Degree of

Bachelor of Science in Chemistry

University of Michigan

Ann Arbor, Michigan

2015

Thesis Advisor: Professor Anne McNeil
ACKNOWLEDGEMENTS

First and foremost, I would like to thank Professor Anne McNeil for giving me the wonderful opportunity to work in her group. I know taking me in as a senior so last-minute was hard, but you were always supportive of me and treated me as a valued member of your lab. Your enthusiasm for your research motivates me to do my best, and it has been a great honor to work in your lab and learn from you. The unconditional support, positivity, and genuine care you show for your students, as well as your dedication to outreach, always inspire me. I wish you and your family all the best in the years to come!

I am also tremendously grateful to Zachary Bryan for his mentorship during this past year. Thank you for your kindness and patience; even when things didn’t turn out the way we expected, you still managed to make the best of the situation. The training I’ve received from you has been one of the most valuable things I’ve learned during my college career. You are truly the best mentor I could ask for, and I wish you all the best in your future endeavors!

Thank you to the rest of the McNeil lab for all their help and support. You guys treated me as a fellow member of the lab, and made me look forward to coming in. Special thank you to Pete Goldberg, Ariana Hall, Gesine Veits, and Kendra Souther for their support, whether it was teaching me how to use lab instruments or giving me helpful suggestions for my project. You guys are the best!

I’d also like to thank my “Chem Cult” friends. Special shout-out to Christina Na and Jenny Berry for helping me get through our chemistry classes in style.

Lastly, I want to thank my roommates Katy Robinson and Maria Laukaitis for always being there for me during these past four years.
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ABSTRACT

Conjugated polymers are a class of organic macromolecules that contain a π-conjugated system in their backbone structure, enabling the absorbance and transport of light. The recent interest in this field can largely be attributed to the discovery that π-conjugated polymers become conductive upon electrochemical doping, which has implications in optoelectronic applications. Compared to current silicon optoelectronic devices, corresponding organic devices offer unique properties such as reduced costs and solution processability onto flexible substrates. Another important benefit of π-conjugated polymers lies in their ability to be tuned via backbone substitution with various substituents.

In 2004, there was a breakthrough with the discovery that the transition-metal-catalyzed polymerization of poly(3-hexylthiophene, P3HT) proceeds through a living, chain-growth mechanism, which was termed catalyst-transfer polycondensation (CTP). CTP allows for more control over polymer sequences in the form of defined end groups and the ability to tune the molecular weight via the monomer/catalyst ratio. However, identifying monomers that proceed through this mechanism requires extensive screening conditions. Moreover, even with polymerizations that proceed through CTP, side reactions such as chain transfer, disproportionation, and termination can occur that result in a loss of control over the resulting polymer sequence.

Identifying novel polymerization conditions that proceed via CTP has proved challenging; therefore, our efforts lie in developing a method that can be applied post-polymerization to purify the polymer samples through end-group functionalization. The purity of the polymers will be analyzed using gel permeation chromatography (GPC) and matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) mass spectrometry (MS). Initial experiments with poly(2,5-dihexoxy-p-phenylene) are promising; however, the low solubility of the polymer chains must be considered.
Functionalized polystyrene resin for isolating conjugated polymers with precise sequences

1. Introduction

Conjugated polymers

Conjugated polymers are a class of organic macromolecules that can absorb and transport light due to the π-conjugation in their backbone structure.\textsuperscript{1-3} The recent interest in this field can largely be attributed to the Nobel Prize award-winning discovery of the high electrical conductivity of polyacetylene, the simplest conjugated polymer\textsuperscript{4} (Chart 1.1). An important benefit of π-conjugated polymers lies in their solution processability, which enables access to optoelectronic devices with unique functionalities, such as mechanical flexibility.\textsuperscript{4} Furthermore, the conductive properties of π-conjugated polymers can be tuned via backbone substitution with various substituents.\textsuperscript{5} Because of these properties, π-conjugated polymers have been studied extensively, and there has been considerable progress in the potential applications of these polymers in organic optical and electronic devices. For example, in 1990, the first polymer-based light emitting diode was created using poly(p-phenylene vinylene) (PPV) (Chart 1.1) in the active layer.\textsuperscript{6}

The conductivities of π-conjugated polymers are comparable to those of both semiconductors and metals. Polyacetylene becomes conductive upon doping with iodine; there have been reports of conductivities\textsuperscript{7} up to 10\textsuperscript{5} S/cm, which is on par with that of copper. The conductivity of polythiophene\textsuperscript{8} (Chart 1.1), a commonly used conjugated polymer due to its high environmental stability and structural versatility, is on the order of 10\textsuperscript{-2} S/cm, placing it in the range of a semiconductor. Other common π-conjugated polymers that have been studied include poly(p-phenylene, PPP), poly(phenylene ethynylene, PPE), and polyfluorene (PF) (Chart 1.1).
Chart 1.1: Common Conjugated Polymers

<table>
<thead>
<tr>
<th>Name and Abbreviation</th>
<th>Chemical Structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polyacetylene</td>
<td><img src="acenetylene.png" alt="Chemical Structure" /></td>
</tr>
<tr>
<td>Poly((p)-phenylene vinylene, PPV)</td>
<td><img src="PPP.png" alt="Chemical Structure" /></td>
</tr>
<tr>
<td>Poly(3-hexylthiophene) (P3HT)</td>
<td><img src="P3HT.png" alt="Chemical Structure" /></td>
</tr>
<tr>
<td>Poly(2,5-dialkoxyp-phenylene, PPP)</td>
<td><img src="PPP.png" alt="Chemical Structure" /></td>
</tr>
<tr>
<td>Poly(2,5-dialkoxyp-phenylene ethynylene, PPE)</td>
<td><img src="PPE.png" alt="Chemical Structure" /></td>
</tr>
<tr>
<td>Poly(9,9-dialkyl fluorine, PF)</td>
<td><img src="PF.png" alt="Chemical Structure" /></td>
</tr>
</tbody>
</table>

*Synthesis of \(\pi\)-conjugated polymers via step-growth polymerization*

Traditionally, \(\pi\)-conjugated polymers have been synthesized via transition-metal-catalyzed step-growth polymerizations, which involve successive reactions between pairs of mutually reactive functional groups. A generic Kumada cross-coupling step-growth polymerization mechanism is depicted in Scheme 1.1. A key feature of this type of polymerization is that large number average molecular weights (\(M_n\)), which is one method of measuring the average molecular weight of the chains in a polymer sample, are only attained at high functional group conversion. Notably, in step-growth polymerizations, reactions occur between any two molecular species whether they are monomers, oligomers, or polymers. For this reason, the resulting measure of distribution of the molecular weight of a polymer sample, known as dispersity (\(D\)) is
relatively high.\(^9\) In summary, with step-growth polymerizations, there is little control over \(M_n, D,\) and/or polymer sequence.

**Scheme 1.1: Mechanism for Step-Growth Polymerization**

![Scheme 1.1: Mechanism for Step-Growth Polymerization](image)

**Synthesis of \(\pi\)-conjugated polymers via controlled chain-growth polymerization**

In 2004, there was a breakthrough when Yokozawa\(^{10}\) and McCullough\(^{11}\) independently discovered that the transition-metal-catalyzed polymerization of P3HT (Scheme 1.2) proceeds through a controlled chain-growth mechanism. Although P3HT had been studied extensively in the field of conductive polymers, these studies were the first to elucidate that the mechanism followed one of chain-growth polymerization.\(^{12}\)
Scheme 1.2: Discovery of CTP

Yokozawa et al.

\[
\begin{align*}
\text{I} & \xrightarrow{1) \text{i-PrMgCl}} \text{Br} \\
\text{C}_6\text{H}_{13} & \xrightarrow{2) \text{Ni(dppp)Cl}_2} \text{S} \\
\end{align*}
\]

McCullough et al.

\[
\begin{align*}
\text{I} & \xrightarrow{1) \text{LDA}} \text{Br} \\
\text{C}_6\text{H}_{13} & \xrightarrow{2) \text{ZnCl}_2} \text{S} \\
\text{Br} & \xrightarrow{3) \text{Ni(dppp)Cl}_2} \text{H} \\
\text{C}_6\text{H}_{13} & \\
\end{align*}
\]

In transition-metal-catalyzed chain-growth polymerizations, a precatalyst activates a monomer in a step known as initiation. During propagation, the catalyst remains associated with the growing chain as the oligomer begins reacting with other monomers to form polymer chains. In the termination step, the formation of reactive intermediates is stopped, which can occur as a result of quenching reactions or full monomer consumption. In chain-growth polymerizations, \(M_n\) growth is linear with respect to conversion, producing lower \(\bar{D}\) values as compared to step-growth polymerizations (Figure 1.1 below). Yokozawa and McCullough’s reports\(^\text{10,11}\) of P3HT chain-growth polymerizations included linear relationships between \(M_n\) and monomer conversion, the ability to control the \(M_n\) via monomer/catalyst ratio tuning, and a unique set of polymer end-groups determined by matrix-assisted laser desorption/ionization (MALDI-TOF) mass spectrometry (MS). Herein, we refer to polymerizations that have these characteristics as “controlled chain-growth polymerizations.”

**Figure 1.1**: Generic \(M_n\) and \(\bar{D}\) versus conversion plots for step-growth and chain-growth
The proposed mechanism through which the controlled chain-growth polymerization of P3HT proceeds is depicted below in Scheme 1.3. It was hypothesized that in the Kumada cross-coupling catalytic cycle, after the reductive elimination step, the metal catalyst remains associated with the growing polymer chain in a “metal-polymer π-complex” (Scheme 1.3.2). In this way, the polymerization proceeds through a controlled chain-growth mechanism that has been termed catalyst-transfer polycondensation (CTP).

**Scheme 1.3: Proposed Mechanism for Chain-Growth Polymerization**

Precatalyst considerations

In this study, the catalyst will be used to introduce end-groups to the polymer. These end-groups are of great significance as they will differentiate the “controlled polymer” from the “uncontrolled polymer.” We will use a derivative of Ni(dppe)BrAr, which has been shown to be superior to Ni(dppe)Cl₂ because of (1) increased solubility due to the presence of the aryl group,¹³ (2) end-group control; as depicted in Scheme
1.4, the aryl group at the metal center becomes the end-group on the polymer chain, and (3) a faster initiation step relative to propagation.\textsuperscript{13} The Ni(dppe)Cl\textsubscript{2} catalyst must undergo two successive transmetallations before it reductively eliminates and becomes part of the catalytic cycle, resulting in a single defect in the polymer chain\textsuperscript{14} (Scheme 1.4a). On the other hand, Ni(dppe)BrAr begins directly in the cycle in the step before transmetallation, making initiation faster relative to propagation (Scheme 1.4b).

**Scheme 1.4:** Initiation Using the Ni(dppe)Cl\textsubscript{2} and Ni(dppe)BrAr Catalysts

Limitations: Competing Side Reactions

In ideal chain-growth polymerizations, each catalyst molecule will begin a polymer chain and remain associated with its respective chain throughout the reaction, creating polymers that are identical in length, sequence, and end-groups. For controlled chain-growth polymerizations, the rates of competing pathways such as chain transfer, disproportionation, and termination are slow relative to initiation and propagation. However, these side reactions can still occur, resulting in a loss of the ability to control $M_n$ via the monomer/catalyst ratio, a loss of defined end-groups, and an increase in $\bar{D}$. Conjugated polymers with precise sequences lead to improved performance; for example, highly regioregular P3HT is needed for higher degrees of crystallinity and improved device performance.\textsuperscript{14} Therefore, isolating the desired polymers is of great importance. However, side products and desired polymers often have similar bulk properties (such as polymer length and chemical reactivity); consequently, isolating these polymers is challenging.

Three common competing reactions encountered in transition-metal-catalyzed chain-growth of conjugated polymers are chain transfer, disproportionation, and termination. In this discussion, we assume a generic aryl group (Ar) as the end-group introduced by the catalyst.
Scheme 1.5: Chain Transfer Products

A depiction of the chain transfer competing pathway is shown above in Scheme 1.5. Chain transfer is observed when the growing polymer chain loses its association with its metal center. The catalyst can either transfer to a monomer or to another polymer chain that has become unassociated with its respective metal catalyst. Chain transfer to monomer results in formation of complexes (a) and (b) (Scheme 1.5). Upon quenching with hydrochloric acid (HCl), (a) will form polymer with hydrogen on both ends (denoted as H/H) while (b) will form polymer (e) with Br/Ar end-groups.

P = Ar, MgCl, or H
On the other hand, chain transfer to a polymer chain can occur, forming complexes (b) and (c). In Scheme 1.5, the new polymer chain that the catalyst becomes associated with is denoted as “P;” the end-group of this polymer ultimately depends on where P originated from. Accordingly, after quenching, (c) will form polymer (e) with the end-groups H/H or H/Ar. In summary, chain transfer can form polymers with H/H, Br/Ar, or H/Ar end-groups.

Scheme 1.6: Disproportionation Products

**Competing Side Reactions: Disproportionation**

The disproportionation competing pathway is depicted in Scheme 1.6 and occurs when two metal catalysts undergo a ligand exchange by swapping polymer chains, forming catalyst (b) (LₙMX₂) and complex (a) (LₙM(polymer)₂) (Scheme 1.6). Upon quenching, (a) will form a polymer (c) with Ar/Ar end-groups. Catalyst (b) is still an active catalyst for chain-growth polymerization; it can initiate a new monomer and upon
quenching, will form a polymer with a single defect (polymer (d)) via the pathway discussed previously (Scheme 1.4a).

**Scheme 1.7: Termination Products**

![Scheme 1.7: Termination Products](image)

**Competing Side Reactions: Termination**

Scheme 1.7 above shows the products that result from the termination competing pathway. Early termination of the polymerization can be attributed to trace amounts of moisture; this causes the polymer to be hydrolyzed, forming polymer (a) and catalyst (b). For polymer (a), further propagation is impossible due to an absence of Br and/or MgBr active ends. As discussed previously, catalyst (b) can initiate a new monomer and will form polymer (c) upon HCl quenching.

In summary, chain transfer, disproportionation, and termination reactions produce polymers with a variety of end-groups (such as H/H, Br/Ar, H/Ar, Ar/Ar, H/Br) and \(M_n\) values, which lead to higher D values. Evidence of these side reactions can be obtained by analyzing polymer end-groups using MALDI-TOF-MS.

**Analysis of end-groups using MALDI-TOF-MS**

MALDI-TOF-MS has been used to identify the end-groups of polymer chains. An example spectrum\(^{15}\) of controlled poly(2,5-dihexyloxy-p-phenylene) (Figure 1.2a) contains peaks that correspond to the molecular weight of the repeat unit. In this
spectra, there is only set of these peaks, revealing that chains with 1,4-diethoxybenzene/H end-groups (controlled polymer) are predominant. Significantly, although the repeat unit is equivalent in the controlled and uncontrolled polymers, the various end-groups will cause a shift in the mass to charge ratio (m/z) of the starting point in the spectrum. This can be observed in the spectrum\textsuperscript{15} of poly(9,9-diocetylfluorene), in which there is indication of products from competing reactions (Figure 1.2b).

**Figure 1.2**: MALDI-TOF-MS of PPP and PF

![MALDI-TOF-MS of PPP and PF](image)

**Limitations of CTP**

Although a number of other conjugated polymers have also been identified as proceeding through CTP in their polymerization,\textsuperscript{11} the search for additional monomers requires extensive screening of polymerization conditions. There has been progress in identifying new catalysts and conditions that result in polymerization via CTP; however, these discoveries have largely been serendipitous and do not have universal applicability. For example, Bryan et al.\textsuperscript{15} found that an N-heterocyclic carbene-ligated palladium catalyst mediated CTP in phenylene- and thiophene- based monomers; however, this was not applicable for a fluorene-based monomer. Furthermore, even with polymerizations that proceed via CTP, competing reactions are still observed. For instance, Huck et al.\textsuperscript{16} reported the presence of uncontrolled polymerization products,
albeit small, even in the controlled chain-growth Suzuki polymerization of fluorene copolymers. Considering the challenges associated with CTP, we believe efforts should be placed in post-polymerization methods to separate controlled and uncontrolled polymers.

Aims

The goal of this project is to develop a simple, post-polymerization method to isolate controlled polymers. We propose to use end-group functionalization to selectively couple the controlled polymers to a polystyrene resin. The uncontrolled polymers can then be removed by washing with solvent, and the controlled polymer can subsequently be decoupled from the resin, producing polymers that will be analyzed by gel permeation chromatography (GPC) and MALDI-TOF-MS.

2. Results and Discussion

The initial approach involved a catalyst that was directly bound to the resin by a linker; a general schematic of this method is shown in Scheme 2.1.

Scheme 2.1: Catalyst-Bound Resin

Using this approach, only controlled polymers would couple to the resin during polymerization. The uncontrolled polymers could subsequently be removed from the insoluble polystyrene resin. After this procedure, the polymer would be cleaved from the resin, isolating the controlled polymers.

Scheme 2.2: Catalyst-Bound Resin Model System
To test this idea, a model system was created in which an ethyl phenyl ether derivative would be attached to the catalyst while the ether side would link to the polystyrene resin (Scheme 2.2a). After polymerization, the desired polymers would be linked to the resin through this ethyl phenyl ether group (Scheme 2.2b). Trifluoroacetic acid (TFA), which has been shown to be selective in cleaving methoxybenzyl groups, would decouple the polymer from the resin to produce controlled polymer chains (Scheme 2.2c). Unfortunately, initial control experiments with 1,4-dimethoxybenzene and 1,4-bis(octyloxy)benzene revealed that the ether groups on the monomers decomposed in the presence of TFA.

The backbone of π-conjugated polymers is often substituted with alkoxy groups to improve solubility. Using TFA would cause unwanted degradation of these ether bonds in addition to cleavage of the polymer from the resin; therefore, the proposal was modified. In our new method, the resin will be introduced post-polymerization by coupling the end-groups from the controlled polymer to polystyrene resin that has been functionalized with a linker. The uncontrolled polymers can subsequently be removed by washing with solvent, and a decoupling reaction can be performed to return the controlled polymer in isolation. A general schematic of this method is shown below in Scheme 2.3.

**Scheme 2.3:** Functionalized Resin Used to Separate Marked Polymers

To begin, monomers for poly(2,5-dihexoxy-p-phenylene) and poly(3-hexylthiophene) were synthesized, as the homopolymers and copolymers of PPP and P3HT have been studied extensively. In our initial studies, we performed a Grignard metathesis reaction of 1,4-dibromo-2,5-bis(hexyloxy)benzene 1 (Scheme 2.4), followed by polymerization using Ni(dppe)Br(o-tolyl) to introduce o-tolyl end-groups. The polymerization was quenched with S₈, producing thiol-capped polymers (P1).
**Scheme 2.4**: Polymerization and Thiol-Capping of PPP Monomer

P1 consisted of a mixture of controlled and uncontrolled polymers. We attempted to isolate the chains with thiol end-groups by coupling P1 to (mercaptomethyl) polystyrene in a one-pot synthesis. In this reaction, P1 was activated with 1-chlorobenzotriazole before forming the non-symmetric disulfide bond between the resin and the polymer. The non-thiol-capped polymers (P1 uncontrolled) were removed via washing and heating in dichloromethane (DCM). The final step involves the use of dithiothreitol (DTT) to cleave the disulfide bond to return the controlled polymer (P1 controlled, Scheme 2.5).

**Scheme 2.5**: Coupling and decoupling of thiol-capped polymer to the resin

According to the literature precedent, the activation using 1-chlorobenzotriazole (Scheme 2.5) was achieved at low temperatures (-78 °C). When we followed this procedure, the cleaving reaction did not produce any polymer; we hypothesized that the problem could be traced back to polymer solubility issues at low temperatures. In our next experiments, the reaction in which the disulfide bond is formed will be performed at room temperature, and we will carefully observe the reaction flask to ensure that the polymer remains in solution.

Because not all the polymer chains contain thiol-end-groups (due to competing pathways), we do not anticipate a full recovery of the polymer after cleavage from the resin. The polymer that has been removed via washing with DCM (P1 uncontrolled, Scheme 2.5) will be analyzed by GPC and MALDI-TOF-MS and compared to P1.
controlled. If our method is successful, we expect a lower $D$ value and the removal of polymers that do not contain thiol-end-groups in the P1 controlled sample.

3. Conclusions and Future Work

The initial proposal involving the catalyst-bound resin was implausible due to decomposition of the ethers on the monomer by TFA. Thus far, the second proposal involving coupling to the resin post-polymerization has a positive outlook. Although low solubility of the polymer chains complicates the procedure, we anticipate that our results will improve if we run the reaction at room temperature.

Scheme 3.1: Summary of Products from Competing Pathways with S$_8$ Quenching

The method described in this study would only isolate polymers with thiol end-groups, but the eventual goal is to isolate polymers with $o$-tolyl/SH end-groups. A summary of the products from competing pathways that result from S$_8$ quenching is presented above in Scheme 3.1. This scheme reveals that some polymers that result from side reactions can still be thiol-capped in the quenching process; therefore, they will not be separated from the polymers with $o$-tolyl/SH end-groups using our current proposed method. In Scheme 3.1, thiol end-groups are colored in red, while non-thiol end-groups are colored in blue; this color coding is transferred to Scheme 3.2, and will be used to explain our future goals.
Future work that involves coupling of the other end of the polymer to the resin will also be explored. The wider scope is to develop a two-stage procedure; the first stage will eliminate polymer that does not contain the thiol-cap at one end, while the second stage will eliminate the polymers that do not have the end-group introduced by the catalyst on the other end. A schematic of these goals is shown above in Scheme 3.2. Stage one will remove the non-thiol-capped polymers (end-groups in blue); the resulting mixture of polymer chains will contain SH/tolyl, Ar/SH, SH/SH, and Br/SH end-groups (end-groups in red). Stage two will remove the polymers that do not contain a tolyl end-group (end-groups in red). The remaining polymer chains will have o-tolyl/SH end-
groups; accordingly, they will be highly precise in sequence. Studies are ongoing in developing stage one; once these experiments are successful, we will move on to stage two experiments.

4. Experimental Procedures and Characterization Data

Materials

Ni(cod)2 and dppe were purchased from Strem. All other reagent grade materials and solvents were purchased from Aldrich, Acros, EMD, or Fisher and used without further purification unless otherwise noted. N-Bromosuccinimide was recrystallized from hot water and dried over P2O5. Compounds S120, S220, S321, S421, S521, S722, S820, R119, and P123 were prepared and characterized according to literature procedures.

General Experimental

NMR Spectroscopy: 1H, 31P, and 13C NMR spectra for all compounds were acquired in CDCl3 as noted on a Varian MR400 or a Varian Inova 500 Spectrometer operating at 500, 202, and 126 MHz, respectively. For 1H, 31P, and 13C NMR spectra the chemical shift data are reported in units of δ (ppm) relative to tetramethylsilane (TMS). 1H and 13C NMR spectra are referenced to residual solvent. Multiplicities are reported as follows: singlet (s), doublet (d), multiplet (m), and triplet (t). All NMR spectra were recorded at rt.

Gel Permeation Chromatography: Polymer molecular weights were determined by comparison with polystyrene standards (Varian, EasiCal PS-2 MW 580-377,400) on a Waters 1515 HPLC instrument equipped with Waters Styragel® (7.8 x 300 mm) THF HR 0.5, THF HR 1, and THF HR 4 type columns in sequence and analyzed with Waters 2487 dual absorbance detector (254 nm). Samples were dissolved in THF (with mild heating) and passed through a 0.2 μm PTFE filter prior to analysis.

Titrations of the Grignard Reagents: An accurately weighed sample of salicylaldehyde phenylhydrazine (typically between 290-310 mg) was dissolved in 5.00 mL of THF. A
0.50 mL aliquot of this solution was stirred at rt while ArMgBr was added dropwise. The initial solution is yellow and turns bright orange at the end point.24

**Gas Chromatography:** Gas chromatography was carried out using a Shimadzu GC 2010 containing a Shimadzu SHRX5 (crossbound 5% diphenyl — 95% dimethyl polysiloxane; 15 m, 0.25 mm ID, 0.25 μm df) column.

**Synthetic Procedures**

![Chemical Structure 1](image1)

**1,4-dihexyloxybenzene (S1):** In a 500 mL flask equipped with a stir bar, hydroquinone (20 g, 0.2 mol, 1.0 equiv) was dissolved in DMF (120 mL). 1-bromohexane (63 mL, 0.45 mol, 2.5 equiv) was added to the flask. The reaction mixture was heated to 80 °C, at which point, with vigorous stirring, potassium carbonate was added (63 g, 0.45 mol, 2.5 equiv). The mixture was vented and continued stirring at 80 °C. On the 4th day, more 1-bromohexane (25 mL, 0.2 mol, 1.0 equiv) was added to the flask. After 5 days, the mixture was cooled to rt. The potassium carbonate was filtered off using a Buchner funnel. The resulting filtrate was poured into water (400 mL) and extracted with hexanes (3 x 200 mL). The organic portions were washed with water (2 x 200 mL) and brine (1 x 200 mL), then dried over anhydrous MgSO4, filtered, and rotovapped. The resultant brown solid was passed through silica gel with CH2Cl2 as the eluent. The resulting eluent was rotovapped and recrystallized from hot methanol to yield 40.557 g of S1 as a white crystalline solid (73% yield).

![Chemical Structure 2](image2)

**1,4-dibromo-2,5-bis(hexyloxy)-benzene (S2):** In a 500 mL flask equipped with a stir bar, dihexyloxy phenylene (22.070 g, 0.79 mol, 1.0 equiv, S1) and chloroform (90 mL) were added sequentially. The mixture was cooled to 0 °C in an ice bath and fitted with
an addition funnel. Bromine (10 mL, 0.20 mol, 2.5 equiv) was added dropwise under N₂ and the pressure was vented through an aqueous solution of 10% Na₂SO₃. After 3 h, the reaction was quenched with an aqueous saturated solution of Na₂SO₃ and vigorously stirred until colorless. The aqueous mixture was extracted with CH₂Cl₂ (3 x 100 mL) and the combined organic layers were washed with water (2 x 100 mL) and brine (1 x 100 mL), then dried over anhydrous MgSO₄, filtered, and rotovapped. The product was recrystallized from CH₂Cl₂-methanol to yield 30.877 g of S₂ as white crystals (89% yield).

\[
\begin{align*}
\text{S}_3: & \quad \text{Sequentially, 3-hexylthiophene (5.00 g, 0.0297 mol, 1.00 equiv) and THF (60 mL) were added to an oven-dried 100 mL Schlenk flask (with a stir bar). The flask was then immersed in an ice bath and stirred under N₂. NBS (13.2 g, 0.0743 mol, 2.50 equiv) was added to the flask. After 2 hours, the reaction was quenched with aqueous saturated Na₂CO₃ (25 mL). The aqueous mixture was extracted with hexanes (3 x 25 mL) and the organic layers were washed with H₂O (2 x 25 mL) and brine (1 x 25 mL), dried over anhydrous MgSO₄, filtered, and concentrated in vacuo to yield a pale yellow oil. This was distilled (106 °C) and passed twice through silica gel in hexanes to yield 0.6255 g of S₃ as a clear oil (6% yield).}
\end{align*}
\]

\[
\begin{align*}
\text{(o-toly)bis(triphenylphosphino)nicke bromide (S4): In the glovebox, Ni(cod)₂ (0.41 g, 1.50 mmol, 1.00 equiv) and PPh₃ (0.831 g, mmol, 2.00 equiv) were dissolved in toluene (7.5 mL) in a 20-mL vial equipped with a stir bar. 2-bromotoluene (0.198 mL, 1.65 mmol, 1.10 equiv) was added and the mixture was stirred for 30 min at rt, at which point hexanes (12 mL) was added. The resultant mixture was then removed from the glove box and the yellow precipitate was collected via filtration and washed with}
\end{align*}
\]
hexanes (15 mL) to yield an orange powder, which was concentrated in vacuo to yield 0.7455 g of S4 (59.9% yield).

(o-tolyl)(1,2-bis(diphenylphosphino)ethane)nickel bromide (S5): In the glovebox, (0.466 g, 0.617 mmol, 1.00 equiv) of (o-tolyl)bis(triphenylphosphino) nickel bromide and dppe (0.270 g, 0.679 mmol, 1.10 equiv) were added to 10 mL of THF in a 20 mL vial. The reaction was stirred for 1 hr at rt. The reaction volume was concentrated in vacuo to an orange powder and recrystallized in THF and hexanes to yield 0.248 g of orange powder (64% yield).

1-chlorobenzotriazole (S7): 1-Benzotriazole (S6, 15 g, 0.12 mol) was dissolved in 100 mL of acetic acid (50% aqueous solution). Under stirring at room temperature, 150 mL of a sodium hypochlorite solution (6% aqueous) was added. After 20 min., the solution was diluted with 100 mL of water. The precipitated white solid was collected via vacuum filtration, then dissolved in dichloromethane and dried over anhydrous magnesium sulfate. The product was concentrated in vacuo and recrystallized from dichloromethane-hexanes to yield 7.2 g (39% yield) of S7 as white crystals.
**Figure S1.** $^1$H NMR spectra for S1. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 6.82 (s, 4H), 3.90 (t, $J = 7.0$ Hz, 4H), 1.75 (m, 4H), 1.45 (m, 4H), 1.34 (m, 8H), 0.90 (m, 6H). * indicates residual H$_2$O, † indicates residual MeOH.
**Figure S3.** $^1$H and $^{13}$C NMR spectra for S3. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 6.78 (s, 1H), 2.50 (t, $J=7.8$ Hz, 2H), 1.55 (m, 2H), 1.33 (br m, 6H), 0.90 (t, $J=6.8$ Hz, 3H). $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 143.3, 131.3, 110.7, 108.3, 31.9, 29.9, 29.8, 29.1, 22.9, 14.4.
Figure S4. $^1$H and $^{31}$P NMR spectra for S3. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.69-7.20 (br, 30H), 7.06 (m, 1H), 6.29 (m, 2H), 5.91 (m, 1H), 2.09 (br, 3H). * indicates residual H$_2$O. $^{31}$P NMR (202 MHz, CDCl$_3$) $\delta$ 22.02 (s).
Figure S5. $^1$H and $^{31}$P NMR spectra for S3. $^1$H NMR (500 MHz, CDCl$_3$) δ 8.20 (m, 4H), 7.73 (m, 2H), 7.62 (m, 9H), 7.31 (m, 2H), 7.09 (m, 2H), 6.72 (m, 2H), 6.56 (m, 2H), 6.41 (m, 1H), 2.40 (m, 2H), 2.22 (s, 3H), 1.63 (m, 2H). * indicates residual H$_2$O, # indicates residual THF, † indicates residual benzene. $^{31}$P NMR (162 MHz, CDCl$_3$) δ 54.48 (d, J = 19.3 Hz), 36.40 (d, J = 17.6 Hz).
**Figure S7.** $^1$H NMR spectra for S7. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.09 (d, 1H, $J = 8.64$ Hz), 7.60 (m, 2H), 7.45 (m, 1H). * indicates residual H$_2$O.

**Polymerization Experiments**

*Representative Procedure for Preparing Monomer for Polymerizations:*

\[
\begin{align*}
\text{S2} & \quad \text{Br} \quad \text{OC}_6\text{H}_{13} \\
\text{C}_6\text{H}_{13}O & \quad \text{Br} \\
& \quad i-\text{PrMgCl} \quad \text{THF} \\
& \quad \text{ClMg} \quad \text{OC}_6\text{H}_{13} \\
& \quad \text{C}_6\text{H}_{13}O \quad \text{Br}
\end{align*}
\]

**S8:** In the glovebox, 1,4-dibromo-2,5-bis(hexyloxy)benzene (1.5 g, 3.4 mmol, 1.0 equiv) was dissolved in 3.6 mL of THF in a 20 mL vial, $i$-PrMgCl (1.8 mL, 3.1 mmol, 0.9 equiv, 1.7 M) was then added. The reaction mixture was stirred at rt overnight. The next day, the monomer mixture was titrated with 0.2830 M phenylhydrazone, and its concentration was calculated to be 0.3825 M.
Representative Procedure for Polymerizations:

PPP: In the glovebox in a 20 mL vial equipped with a stir bar, (o-tolyl)(1,2-bis(diphenylphosphino)ethane)nickel bromide (8.8 mg, 0.014 mmol, 1 equiv) was dissolved in 8.2 mL of THF. The monomer mixture (1.83 mL, 0.700 mmol, 50 equiv, S8 in THF, concentration determined by titration) was added and the reaction was stirred at rt for 4.5 hours. A 1 mL aliquot of the 10-mL reaction mixture was quenched with concentrated HCl (1 mL) (P2). For the rest of the reaction mixture, S8 (248 mg, 7.74 mmol) and DBU (0.14 mL, 0.97 mmol) was added and stirred for 30 mins in the glovebox. 5 mL of concentrated HCl was then added to the mixture (P1). Both samples were extracted with dichloromethane and concentrated in vacuo.

Representative GPC Data:

<table>
<thead>
<tr>
<th>Sample</th>
<th>Mn (kDa)</th>
<th>Dispersity</th>
</tr>
</thead>
<tbody>
<tr>
<td>P1</td>
<td>21.4</td>
<td>2.02</td>
</tr>
<tr>
<td>P2</td>
<td>18.6</td>
<td>1.76</td>
</tr>
<tr>
<td>Theoretical</td>
<td>13.8</td>
<td>--</td>
</tr>
</tbody>
</table>

Coupling and decoupling to resin

Representative Procedure for Coupling to Resin:
**R1:** In an oven-dried 25-mL Schlenk flask equipped with a stir bar, 1-chlorobenzotriazole (3.7 mg, 0.024 mmol, 1.5 equiv) and benzotriazole (1.9 mg, 0.016 mmol, 1 equiv) were dissolved in CH$_2$Cl$_2$ (0.2 mL) under N$_2$. The solution was cooled to -78 °C, and a solution of thiol-capped PPP polymer (est. 320 mg, 0.016 mmol, 1 equiv) dissolved in CH$_2$Cl$_2$ (2 mL, with heating) was added dropwise to the reaction mixture, which turned a milky white and increased in viscosity. The mixture was stirred for 2 hours. Mercaptomethyl resin (110 mg, 0.48 mmol at 4.0 mmol/g S loading, 30 equiv) was then added slowly at -10 °C. The reaction was left stirring overnight under N$_2$ while it warmed slowly to rt. The next day, the reaction mixture was filtered; the thiol resin was collected and heated in ~5 mL of DCM, then filtered a second time. The combined filtrate portions were quenched with sodium sulfite (0.1 g in 2 mL water) and saturated sodium bicarbonate (4 mL), then extracted with DCM and concentrated in vacuo. The collected resin (~60 mg) was stored in the fridge.

*Representative Procedure for De-coupling from Resin:*

![Reaction Scheme](image)

**P1 controlled:** In a 20 mL vial with a stir bar, the thiol resin (CZ-i-135) was heated in ~5 mL of DCM. Dithiolthreitol (DTT, 12.3 mg, 0.08 mmol, 5 equiv) was dissolved in the mixture, and the reaction was stirred for 30 minutes at rt. The mixture was filtered and the resin collected, the resin was then heated in DCM and filtered again. The combined filtrates were extracted with dichloromethane and concentrated in vacuo; however, no polymer was collected.
5. References