CHEMICAL OXIDATIVE POLYMERIZATION VS. GRIGNARD METATHESIS

POLYMERIZATION OF ELECTRON-RICH THIOPHENE-BASED POLYMERS

by

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HONORS THESIS

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DEDICATION

This thesis is dedicated to my late cousin Mathelle. Her life was filled with chasing the challenge, which will forever inspire me to do the same.

ACKNOWLEDGEMENTS

There are several people I would like to acknowledge that have helped me throughout this journey thus far. I would like to first mention Dr. Jennifer Irvin for taking a chance on me and helping me realize my potential, as well as for being the most supportive, kind, genuine leader I have ever had the privilege to work under. Little did I know the experiences being in research had in store for me and I'll always be grateful she gave me the opportunity to find out.

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As enthusiastic and passionate about his research as David Hebert was, it always helped me understand the bigger reasons for why we were doing this. I appreciate him for

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ABSTRACT

Conductive polymers are long chains of organic molecules that contain a conjugated structure consisting of alternating single and double bonds. Introduction of an electric field causes these polymers to change color, volume, conductivity, reactivity, and solubility. This ability has led to applications including sensors, energy conversion and storage, actuators, and display technologies. Conductive polymers can be functionalized with disease-specific biomolecules, producing an electrochemical response in the presence of genetic markers for diseases such as cancer and Parkinson's Disease. Identifying inherited predisposition for diseases leads to early detection, which increases success of treatment.

We have synthesized soluble, electron-rich conductive polymers derived from thiophene. Two monomers were synthesized: 3,4-bis(hexyloxy)thiophene (BHOT, a symmetrical thiophene to help prevent specific defects), and 2,5-dibromo-3,4-bis(hexyloxy)thiophene (Br2BHOT). These monomers were prepared, purified using column chromatography, and characterized using nuclear magnetic resonance (NMR) spectroscopy. The monomers were polymerized along with 3-hexylthiophene (3HT, a monomer used as a baseline standard for comparison) using various polymerization techniques. Both Grignard metathesis (GriM) and chemical oxidative polymerization methods were used to produce conductive polymers. Gel permeation chromatography (GPC) was used to compare molecular weights and degrees of polymerization of polymers obtained from both methods. The best results were obtained for both polymers

when using standard addition (adding oxidant to monomer), 4 eq. of $FeCl_3$, and 24 hours for chemical oxidative polymerization.

While the applications of conductive polymers are promising, soluble polymers with high molecular weights are needed to enable their use in most potential applications. As chain length/molecular weight increase in conductive polymers, the polymers become more mechanically robust and more conductive, making them more useful in energy storage or biosensors.

I. BACKGROUND/MOTIVATION

Background

Conductive polymers are long chains of organic molecules that contain an unusual, conjugated structure consisting of alternating single and double bonds, which encompasses all conductive polymers. Introduction of an electric field causes these polymers to change color, volume, conductivity, reactivity, and solubility. This ability has led to applications including sensors, energy conversion and storage, actuators, and display technologies.

Conventional energy sources are rapidly depleting day by day, leading to the need for renewable energy sources such as solar, wind and hydroelectricity.[1] Solar energy is a viable alternative, but dominating technology utilizes crystalline silicon photovoltaic modules which are generally more expensive to produce than traditional grid power.[2] Competitive materials such as organic solar cells are being developed to help bring down the cost of photovoltaic modules and make solar energy not only energy-efficient, but cost-efficient as well. Solar cells made from conductive polymers are especially promising because they can be flexible and lightweight.[3]

Another application for conductive polymers is in biosensors.[4] Conductive polymers can be functionalized with disease-specific biomolecules, producing an electrochemical response in the presence of genetic markers for diseases such as cancer and Parkinson's Disease.[4] Identifying inherited predisposition for diseases leads to early detection, which increases success of treatment.

While the applications of conductive polymers are promising, soluble polymers with high molecular weights (the product of polymer chain length, n, and the molecular

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weight of the repeat unit) are needed to enable their use in most potential applications.[5] As chain length/molecular weight increase in conductive polymers, the polymers become more mechanically robust and more conductive, making them better for use in organic solar cells or biosensors.

Motivation

The overall goal is to understand how changes in chemical structure affect polymerization and what molecular weights are achievable. The conductive polymers that are used are derived from thiophene. Addition of ether substituents increases electron density, reducing oxidation potential and increasing polymer electrochemical stability.[5] Long alkyl chains are incorporated to impart solubility, which aids in polymer processing. Different polymerization techniques are tested on the same monomer to determine which produces the highest molecular weight polymers.

The two polymerization methods that are sought after in this thesis are chemical oxidative polymerization and Grignard Metathesis. Chemical oxidative polymerization (COP) is historically regarded as the first recognized method to generate conductive polymers.[6] This reaction is typically done in solution, however it is able to be carried out in the gas or solid phase as well.[7] Due to the quick and simple preparation for the synthesis of conductive polymers, COP is considered an appealing method of choice. However, for monomers that contain sensitive functional groups, this method is not appropriate because of the excessive oxidizing reaction conditions.[6] In addition, contamination with substantial amounts of oxidant (metal) encompasses the polymers produced through COP which is unsuitable for delicate applications unless thorough

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purification is performed. Finally, the propagating species in COP are in the oxidized state, which is less soluble due to double bonds between rings preventing rotation. Poor solubility of the oxidized species typically limits molecular weight for polymers prepared via COP. An example of the mechanism for COP is further illustrated in Figure 1.
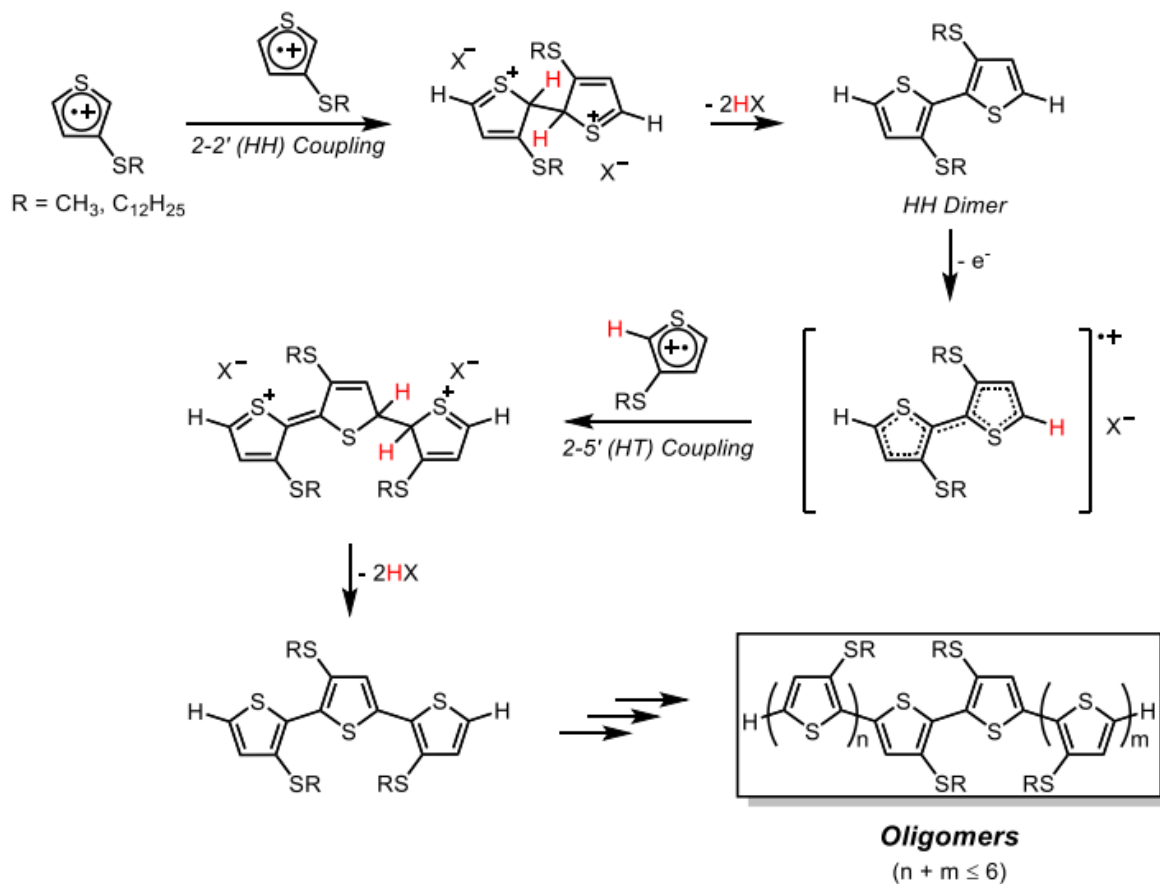
Figure 1: Oxidative polymerization of 3-alkylsulfanylthiophenes.[8]

Grignard Metathesis (GRIM) on the other hand, is a promising polymerization method for several reasons: the convenience of the standard reaction time; it results in increased order (regioregularity) in polymer structure, which enhances conductivity; and

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lower amounts of metal used in the reaction may be important for biomedical

applications.[9] In addition, the polymer is synthesized in the more soluble neutral state

rather than the less soluble oxidized state, potentially leading to higher molecular

weights. However, carrying out the GRIM reaction is not as quick and simple as COP

because of the water sensitive nature of the reaction. Any moisture introduced into the

reaction could have undesirable effects on polymer formation. In addition, monomers

used in this reaction must be highly purified to attain high molecular weights due to the

nature of the reaction as a transition metal-mediated reaction, otherwise impurities

present chain-terminating groups.[6] An example of the mechanism for GRIM is further

illustrated in Figure 2.
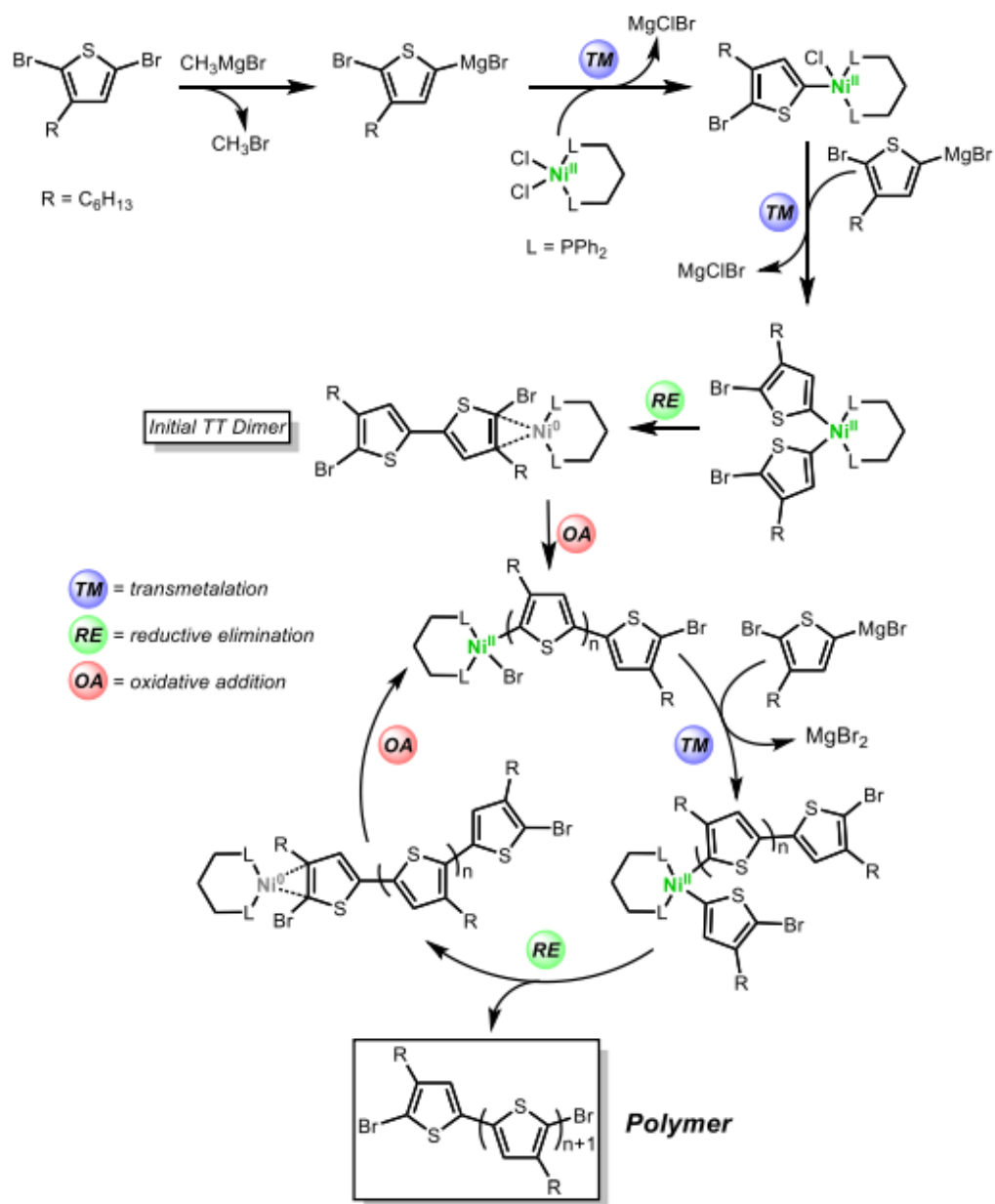
Figure 2: Grignard Metathesis mechanism.[6]

II. RESEARCH

Methods

For this research project soluble, electron-rich conductive polymers derived from thiophene were synthesized. This required synthesis of two different monomers and polymerization of them using various polymerization techniques. The monomers that were prepared were 3,4-bis(hexyloxy)thiophene (BHOT, a symmetrical thiophene to help prevent specific defects; Scheme 1) and 2,5-dibromo-3,4-bis(hexyloxy)thiophene (Br$_2$BHOT; Scheme 2). Once the monomers were made, they were polymerized in addition to 3-hexylthiophene (3HT) which was used as a baseline comparison, using COP (Schemes 3, 4, 6, and 7) and GRIM (Schemes 5 and 8). Variations of COP were performed, including reverse addition and standard addition. Reverse addition occurs when the monomer is added to the oxidant, while standard addition occurs when the oxidant is added to the monomer. This research was aided by other undergraduate researchers, Emma Murphy and Venus Stanton, who have already polymerized BHOT and 3HT using COP, and is a continuation of former graduate student David Hebert's research.

Monomer Synthesis

BHOT Synthesis
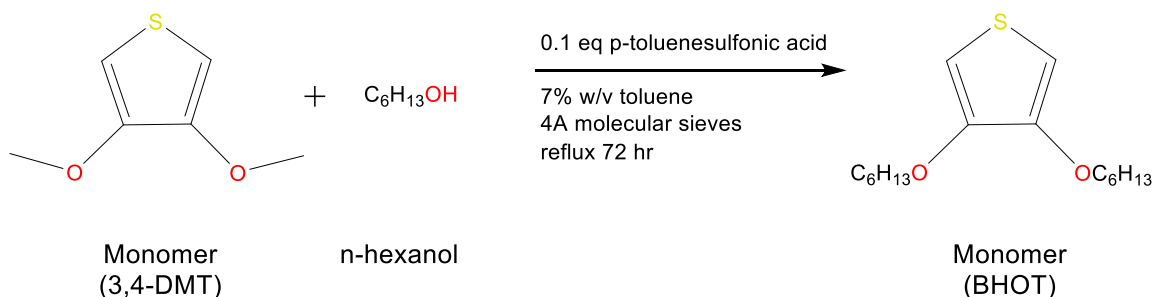
Scheme 1: Monomer synthesis of BHOT via transetherification between 3,4-

dimethoxythiophene (3,4-DMT) and n-hexanol.

BHOT was synthesized by David Hebert as follows. A three-neck round bottom
flask was connected to a Soxhlet extractor containing a cellulose thimble filled with
activated 4Å molecular sieves. A high efficiency condenser was fitted with a gas adapter
connected to a bubbler and added to the extractor, and the remaining two necks of the
flask were fitted with a gas inlet adapter and a septum; a magnetic stir bar was added to
the flask.[6] Toluene (100 mL) and *p*-toluenesulfonic acid (0.39580 g, 20.81 mmol) were
added to the flask, and the mixture was heated at 60 °C under argon with stirring. After 5-
10 minutes, *n*-hexanol (5.78 mL, 46.39 mmol) was added via syringe through the septum
cap. 3,4-Dimethoxythiophene (2.998 g, 20.80 mmol in 5 mL of toluene) was added
slowly via syringe through the septum cap. The reaction was stirred at 130 °C under
argon for 36 hours. The mixture was then allowed to cool to room temperature and
transferred to a 500 mL separatory funnel where it was washed three times with water (60
mL each), once with sat. aqueous $NaHCO_3$ (60 mL), and once more with water (60 mL).
The organic layer was dried over anhydrous $MgSO_4$ and vacuum filtered through a fritted
filter. The filtrate was concentrated under reduced pressure to yield the crude product as a
brown oil. Short-path vacuum distillation was then used to purify the crude product and
yield 4.51 g (76.2%) product as a light-yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 6.16 (s,
2H), 3.98 (t, 4H), 1.81 (p, 4H), 1.44 (p, 4H), 1.33 (sx, 4H), 0.90 (t, 6H) (Figure 3).
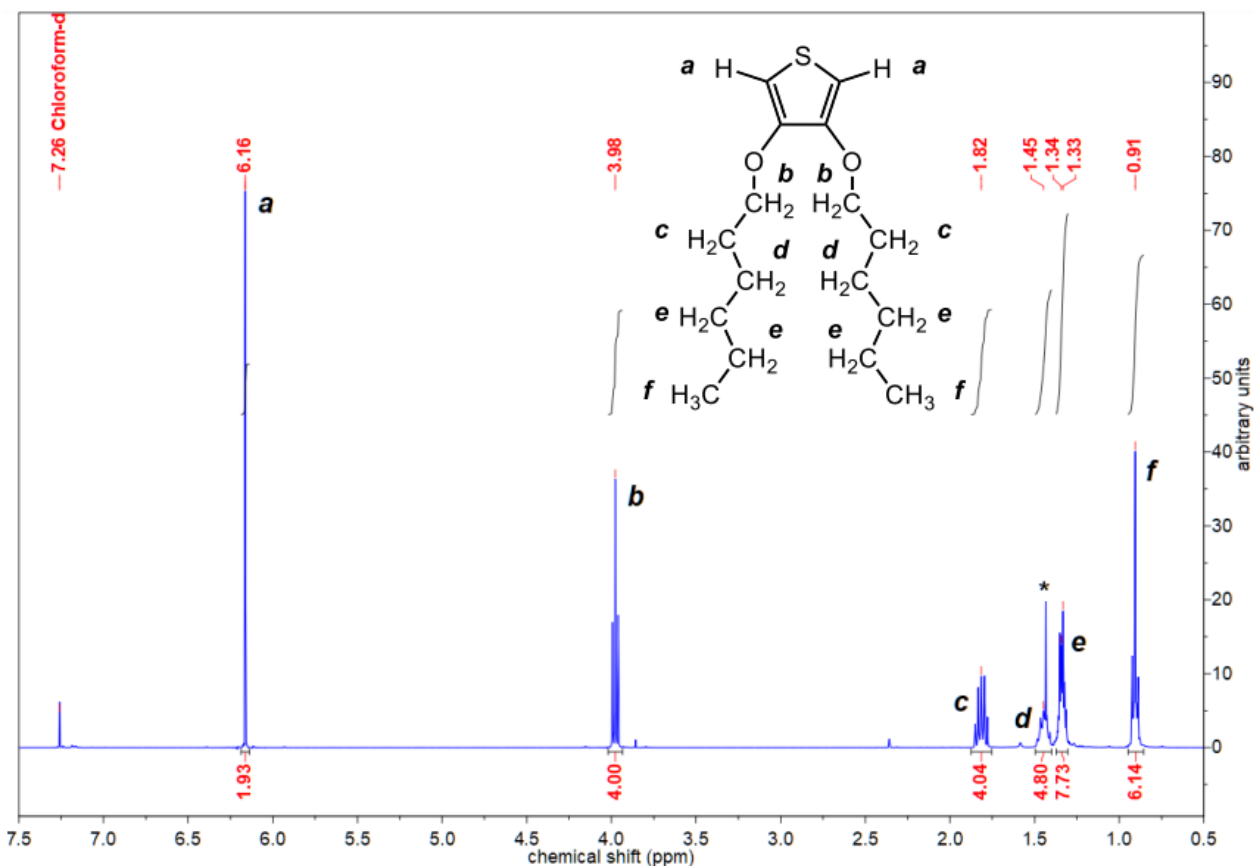
Figure 3: ^{1}H NMR spectrum illustrating BHOT in CDCl₃ synthesized by David Hebert.[6] Each peak shown and labeled corresponds to different sets of protons (hydrogens) that are found and labeled on the BHOT compound. However, the peak with the '*' label refers to cyclohexane.[6]

Br₂BHOT Synthesis
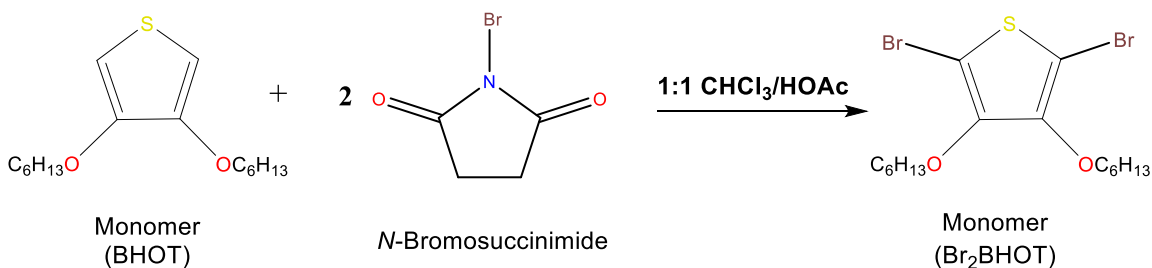
Scheme 2: Monomer synthesis of Br₂BHOT via bromination of BHOT using *N*-bromosuccinimide (NBS).

BHOT was next used in the synthesis of Br₂BHOT. The apparatus used was a

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three-neck round bottom flask outfitted with two gas adaptors and a magnetic stir bar. The apparatus pieces were dried in an oven over night to remove as much moisture as possible before the reaction. The apparatus was set up next to the oven the day of the reaction and then transferred to hood, where it was flushed with argon for 5 minutes prior to adding starting materials. A 1:1 solution of chloroform and glacial acetic acid (16 mL each for a total of 32 mL) was added to the flask against positive argon flow. BHOT (0.50055 g, 1.76 mmol) was added with stirring under positive argon flow. *N*-Bromosuccinimide (0.68822 g, 3.782 mmol) was added slowly over 12 minutes under positive argon flow. The reaction was then protected from light by wrapping in aluminum foil and turning off the hood light. The reaction was left to stir for 1.5 hr, then the crude product was transferred to a 100 mL separatory funnel where it was washed two times with water (25 mL each), two times with sat. aqueous $NaHCO_3$ (25 mL each), and once more with water (25 mL). The organic layer was dried over anhydrous $MgSO_4$ and vacuum filtered through a fritted funnel to collect the crude product in a 250 mL Erlenmeyer flask. The filtrate was concentrated under reduced pressure to yield the crude product as a brown oil. The product was left under high vacuum overnight. A 14:1 solution of hexane and ethyl acetate was used as the eluent to purify the crude product by column chromatography and yield 0.53037 g (68.18%) product as a light-brown oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 4.13 (t, 4H), 1.72 (p, 4H), 1.33 (sx, 4H), 0.90 (t, 6H) (Figure 4).
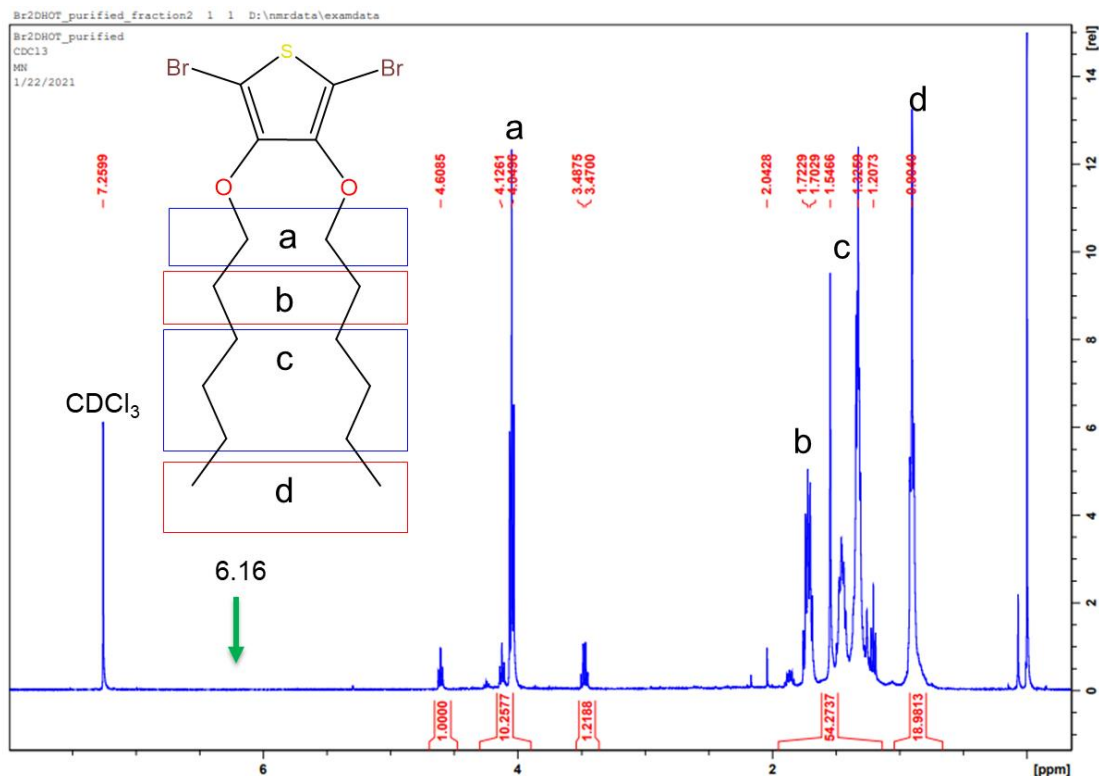
Figure 4: ^{1}H NMR spectrum illustrating Br$_2$BHOT in CDCl$_3$. Each peak shown and labeled corresponds to different sets of protons (hydrogens) that are found and labeled on the Br$_2$BHOT compound. The peaks not labeled indicate impurities still present in the compound. The absence of a peak at 6.16ppm (as seen in Figure 3 for BHOT) indicates that bromination was successful.

Polymerizations

P3HT was used as a baseline comparison to PBHOT, and both the reverse and

standard addition COPs of 3HT, as well as GRIM, were performed.

P3HT - Reverse addition, 2.3 eq. FeCl$_3$ (24 hours)
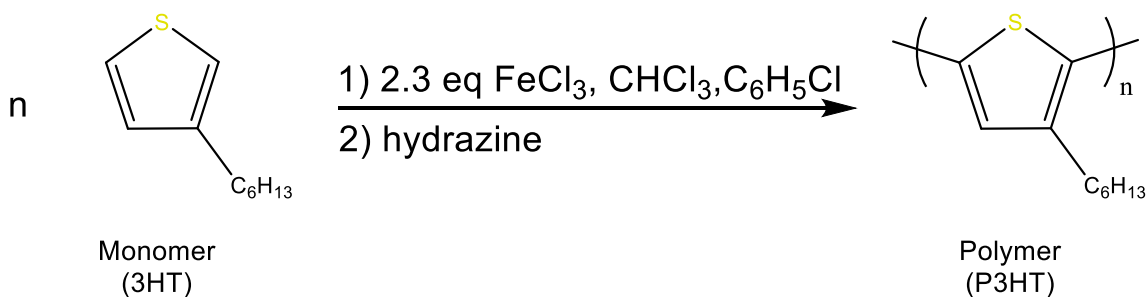
Scheme 3: Polymer synthesis of poly(3-hexylthiophene) (P3HT) via chemical oxidation of 3-hexylthiophene.

The reverse addition chemical oxidative polymerization of 3HT was synthesized by David Hebert as follows. A Schlenk flask was fitted with a gas adaptor connected to a bubbler and a magnetic stir bar was added. Anhydrous $FeCl_3$ (2.3 molar equivalents, 0.525 g, 3.2 mmol) was quickly added to the flask.[6] The mixture was left under argon with stirring and chlorobenzene (30 mL) was added via syringe through the septum cap. After 3-5 minutes, a monomer solution of 3-hexylthiophene (0.25 mL, 1.4 mmol) in chlorobenzene (6 mL) was then added dropwise via syringe. Once the monomer solution was added, a dark green color took over the reaction mixture. The reaction stirred at room temperature under argon for 24 hours. The polymer was precipitated through dropwise addition of the reaction mixture into stirred methanol (250 mL). The polymer/methanol mixture was vacuum filtered through paper in a Büchner funnel and methanol was used to thoroughly wash the polymer. Chloroform (25 mL) was used to resuspend the polymer under argon and the polymer was reduced through the addition of anhydrous hydrazine (0.03 mL, 0.96 mmol) via syringe through the septum cap. The polymer was purified and collected using the methanol precipitation and vacuum filtration methods described above. A yield of 0.893 g (64.4%) of product was obtained as a dark red powder.

P3HT - Standard addition, 2.3 eq. FeCl₃ (24 hours)

| Monomer | | Polymer |
| (3HT) | | (P3HT) |

Reaction conditions: 1) 2.3 eq $FeCl_3$, $CHCl_3$, C_6H_5Cl 2) hydrazine

Scheme 3: Polymer synthesis of poly(3-hexylthiophene) via chemical oxidation of 3-hexylthiophene.

The standard addition chemical oxidative polymerization of 3HT was synthesized by David Hebert as follows. A Schlenk flask was fitted with a gas adaptor connected to a bubbler and a magnetic stir bar was added. Anhydrous $FeCl_3$ (0.521 g, 3.2 mmol) was mixed with acetonitrile (ACN, 5 mL) to make an oxidant solution that was then added dropwise via syringe through the septum cap to a stirred solution under argon, containing 3-hexylthiophene (0.25 mL, 1.4 mmol) in chlorobenzene (30 mL).[6] A dark green color slowly formed in the reaction mixture. The reaction stirred at room temperature under argon for 24 hours. The reaction mixture was precipitated and filtered using the same method described above for reverse addition. Once polymer was collected, chlorobenzene (40 mL) was used to resuspend the polymer and then anhydrous hydrazine (0.04 mL) was added via syringe. The hydrazine addition facilitated a dark blue to violet color change in the reaction mixture. The reaction stirred at room temperature under argon for another 24 hours. The polymer was precipitated and isolated as described above. A yield of 0.604 g (43.6%) of product was obtained as a dark red powder.

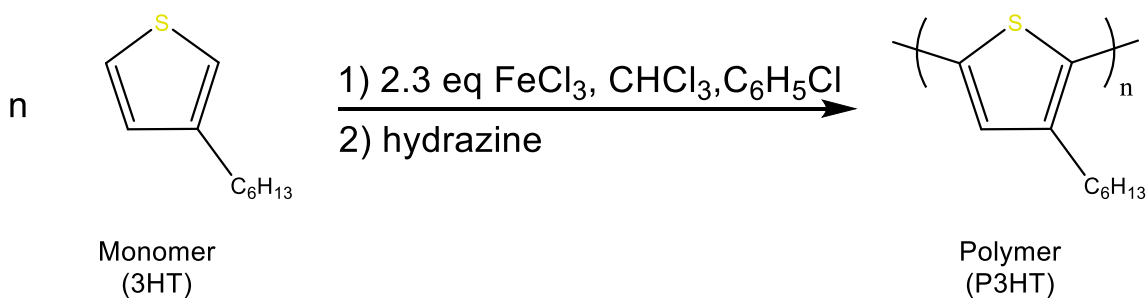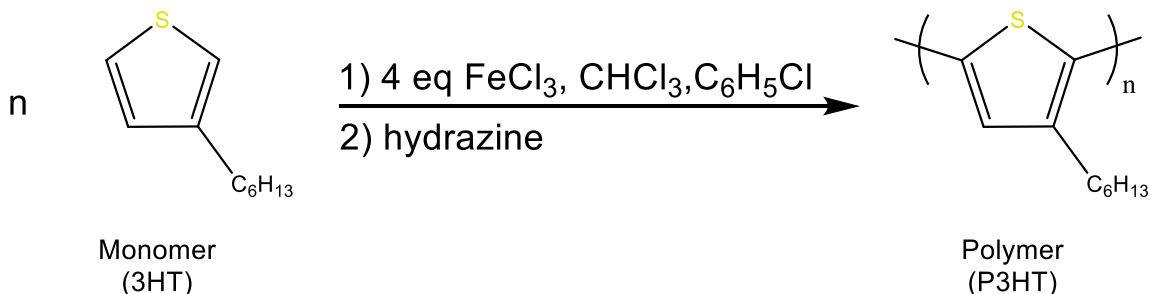*P3HT - Standard addition, 4 eq. FeCl₃ (24 hours)*

Scheme 4: Polymer synthesis of poly(3-hexylthiophene) via chemical oxidation of 3-hexylthiophene.

The standard addition chemical oxidative polymerization of 3HT was synthesized by Emma Murphy as follows. Before 3HT was polymerized, it was purified by first filling a fritted glass filter halfway with silica gel and then passing pure dichloromethane (DCM) through with vacuum filtration. 3HT was passed through the filter and rinsed with DCM. The filtrate was concentrated under reduced pressure and the purified 3HT was left under high vacuum overnight. The apparatus pieces were dried in an oven over night to remove as much moisture as possible before attempting the reaction. A Schlenk flask was fitted with a gas adaptor connected to a bubbler and a magnetic stir bar was added. Purified 3HT (0.26754 g) was added against positive argon flow and chlorobenzene (10 mL) was added to the Schlenk flask via syringe through the septum cap and left to stir. More chlorobenzene (20 mL) was added directly to the Schlenk flask. Anhydrous $FeCl_3$ (1.03156 g, 4 mol) was quickly added to a vial and capped. Acetonitrile (5 mL) was added to dissolve the $FeCl_3$ via syringe through the septum cap and solution immediately darkened. The $FeCl_3$ dissolved in ACN was added slowly via syringe through the septum cap. Septum cap was switched for glass stopper and the reaction stirred at room temperature under argon for 24 hours. The polymer was precipitated and collected using the same method described above in the reverse addition procedure. The oxidized polymer was dissolved in chlorobenzene (40 mL) and added to the Schlenk flask. Anhydrous hydrazine (0.05103 mL) was added via syringe through the septum cap and the reaction mixture started to take on a red/orange color. The reaction stirred at room temperature under argon for another 24 hours. The polymer was precipitated and collected using the same method described above in the reverse addition procedure. However, the polymer was strongly adhered to the filter paper after letting it dry under

high vacuum overnight and was dissolved in chloroform. The chloroform was concentrated under reduced pressure. A yield of 0.03640 g (24.88%) of P3HT was obtained as a dark red solid.

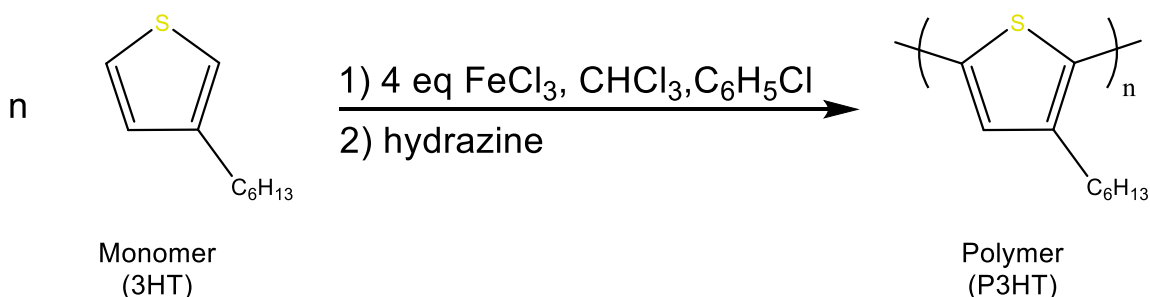*P3HT - Standard addition, 4 eq. FeCl₃ (48 hours)*

Scheme 4: Polymer synthesis of poly(3-hexylthiophene) via chemical oxidation of 3-hexylthiophene.

The standard addition chemical oxidative polymerization of 3HT was synthesized by Venus Stanton as follows. A Schlenk flask was fitted with a gas adaptor connected to a bubbler and a magnetic stir bar was added. The apparatus pieces were dried in an oven over night to remove as much moisture as possible before attempting the reaction. 3HT (0.25190 g, 1.5 mmol) was added against positive argon flow and chlorobenzene (30 mL) was added via syringe through the septum cap to a stirred solution under argon. Anhydrous $FeCl_3$ (0.9732, 6 mmol) was quickly added to a vial and capped. ACN (5 mL) was added via syringe through the septum cap to the $FeCl_3$ and the solution immediately darkened. The reaction stirred at room temperature under argon for 48 hours. The polymer was then precipitated and collected using the same method described above in the reverse addition procedure. The oxidized polymer was resuspended in chlorobenzene (40 mL), and anhydrous hydrazine (0.048 g, 1.5 mmol) was added to the reaction flask via syringe through the septum cap. The reaction stirred at room temperature under argon

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for 48 hours. The polymer was precipitated and collected using the same method

described above. The polymer was dissolved off the filter paper with chloroform into a

vial. The chloroform was concentrated under reduced pressure to dryness. A yield of 49.6

mg (19.69%) of P3HT was obtained as a dark red solid.

P3HT – Grignard Metathesis
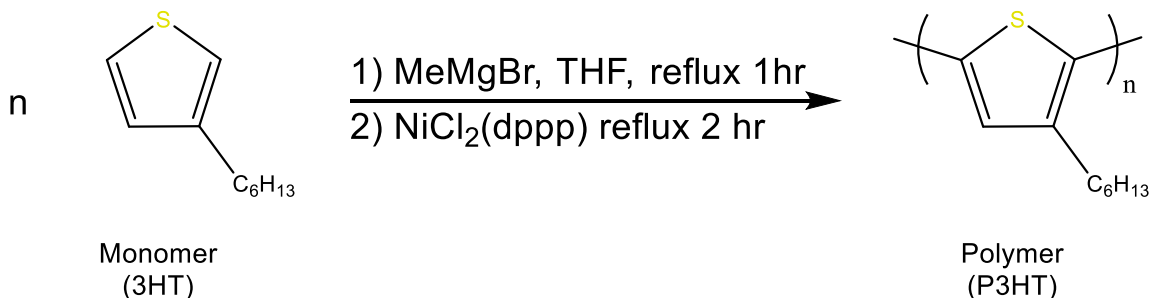
Scheme 5: Polymer synthesis of poly(3-hexylthiophene) via Grignard metathesis of 3-hexylthiophene.

The 3HT polymerized by Grignard Metathesis was synthesized by David Hebert

as follows. A 250 mL three-neck round bottom flask was connected to a reflux condenser

and fitted with a gas adapter connected to a bubbler. The remaining two necks of the

flask were fitted with a gas inlet adapter and a septum; a magnetic stir bar was added to

the flask.[6] 2,5-dibromo-3-hexylthiophene (0.75 mL, 3.5 mmol) was added to the flask

and THF (10 mL) was added, both via syringe through the septum cap. The monomer

solution was stirred and methylmagnesium bromide (1.2 mL, 3.0 M in Et_2O) was

transferred to the flask via argon-purged syringe. The reaction was left to reflux under

argon for 1 hr. $NiCl_2$(dppp) (0.0189 mg, 34.9 μmol) was then introduced against positive

argon flow and the reaction was left to reflux with stirring for another 2 hours. The

reaction took on a red color during this time. The reaction mixture was removed from

heat and allowed to cool to room temperature and added dropwise to stirred methanol

(100 mL). Vacuum filtration was then used to collect the polymer and was further dried

under high vacuum in a desiccator overnight. A yield of 0.308 g (53%) of polymer was

obtained and resembled a glossy dark red solid.

PBHOT – Reverse Addition, 2.3 eq. FeCl$_3$ (24 hours)
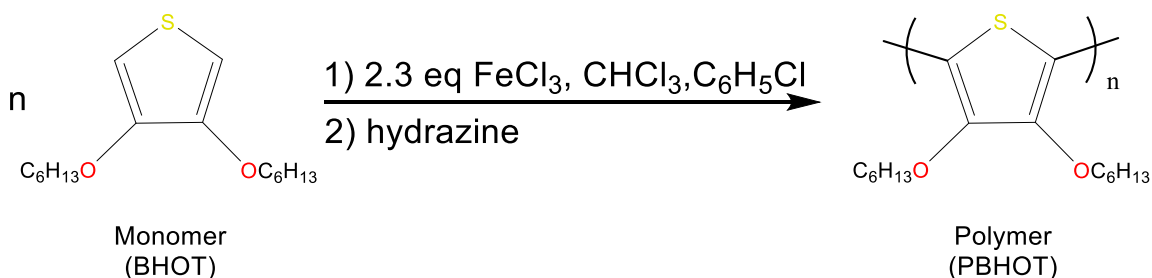
Scheme 6: Polymer synthesis of poly(3,4-bis(hexyloxy)thiophene) via chemical oxidation
of 3,4-bis(hexyloxy)thiophene.

The reverse addition chemical oxidative polymerization of BHOT was

synthesized by David Hebert as follows. A Schlenk flask was fitted with a gas adaptor

connected to a bubbler and a magnetic stir bar was added. Anhydrous FeCl$_3$ (0.295 g, 1.8

mmol) was added and chlorobenzene (30 mL) added via syringe through the septum cap,

with stirring.[6] BHOT (0.21989 g, 0.25 mL, 0.77 mmol) made into a solution with

chlorobenzene (6 mL) and was added dropwise via syringe. The reaction solution took on

a dark greenish/blue hue once the monomer solution was added. The reaction stirred at

room temperature under argon for 24 hours. The polymer was further precipitated and

collected similarly to the methods described above in the P3HT – Reverse Addition, 2.3

eq. FeCl$_3$ protocol. Chlorobenzene (35 mL) was used to resuspend the polymer and then

anhydrous hydrazine (0.03 mL) was added via argon-purged syringe through the septum

cap. The mixture was left to stir at room temperature under argon for another 24 hours.

The polymer was then precipitated and collected using the same method described above.

A yield of 0.0924 g (42.33%) of polymer was obtained and resembled a crimson red
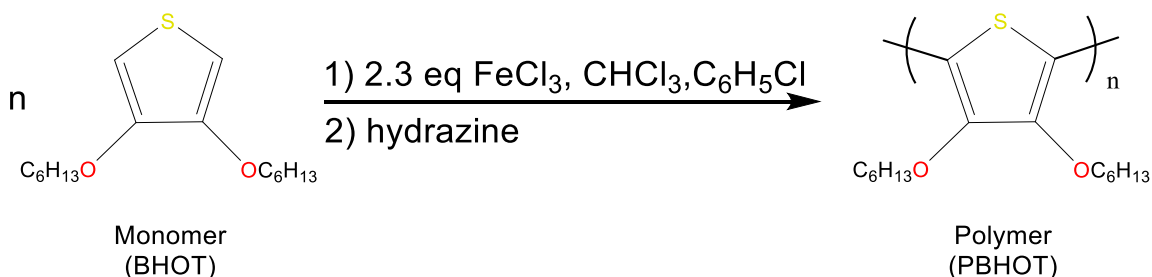
powder.

Scheme 6: Polymer synthesis of poly(3,4-bis(hexyloxy)thiophene) via chemical oxidation
of 3,4-bis(hexyloxy)thiophene.

The standard addition chemical oxidative polymerization of BHOT was

synthesized by David Hebert as follows. A Schlenk flask was fitted with a gas adaptor

connected to a bubbler and a magnetic stir bar was added. BHOT (0.251 g, 0.285 mL,

0.88 mmol) was added against positive argon flow and made into a solution with

chlorobenzene (30 mL) with stirring under argon.[6] Anhydrous FeCl₃ (0.32973 g, 2 mmol)

was quickly added into a glass vial and flushed with argon. Acetonitrile (5 mL) was used

to dissolve the FeCl₃, and the resultant solution was added dropwise via syringe through

the septum cap. Upon addition of the oxidant, the mixture took on a red hue immediately

and further darkened to violet before transitioning to a dark green. The mixture stirred at

room temperature under argon for 24 hours. The reaction mixture was precipitated and

collected similarly to the method described above in the P3HT – Standard Addition, 2.3

eq. FeCl₃ protocol. Chlorobenzene (35 mL) was used to resuspend the polymer and

anhydrous hydrazine (0.03 mL) was added via argon-purged syringe. However, methanol

alone turned out to be enough to reduce the polymer as noted by the red color transition

occurring at the precipitation step. The mixture was stirred at room temperature under

argon for another 24 hours. Isolating the reduced polymer through precipitation straight

from the reaction failed and was instead concentrated under reduced pressure to remove

the solvent and isolate the polymer. A yield of 0.1945 g (78.1%) of polymer was obtained

and resembled a murky oily product.

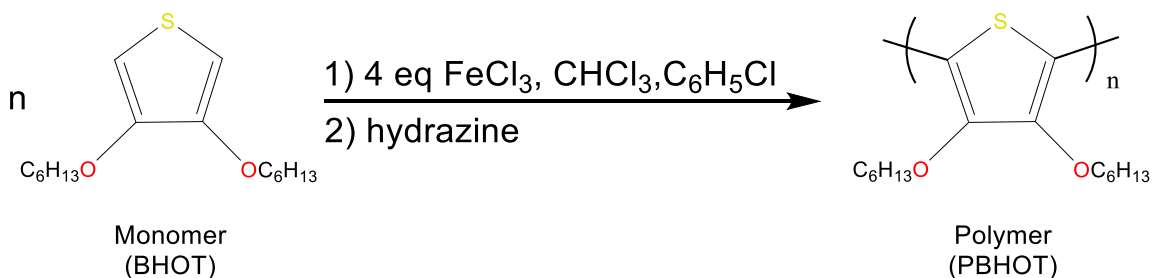*PBHOT – Standard Addition, 4 eq. FeCl$_3$ (24 hours)*

Scheme 7: Polymer synthesis of poly(3,4-bis(hexyloxy)thiophene) via chemical oxidation
of 3,4-bis(hexyloxy)thiophene.

The standard addition chemical oxidative polymerization of BHOT was

synthesized by David Hebert as follows. A Schlenk flask was fitted with a gas adaptor

connected to a bubbler and a magnetic stir bar was added. BHOT (0.205 g, 0.72 mmol)

was added with chlorobenzene (30 mL) to the flask and stirred under argon. Anhydrous

FeCl$_3$ (0.4666 g, 2.9 mmol) was quickly added to a glass vial, flushed with argon, and

ACN (5 mL) was added via syringe through the septum cap to the vial. The resultant

solution was added dropwise via syringe to the reaction flask. Upon the addition of the

FeCl$_3$ solution, the mixture immediately turned red, following with dark green settling in.

The reaction mixture was left to stir at room temperature under argon for 24 hours.

Methanol (250 mL) at -78 °C was used to precipitate the polymer through dropwise

addition of the reaction mixture. The polymer was vacuum filtered through paper using a

Büchner funnel, and chlorobenzene (35 mL) was used to resuspend the polymer.

Anhydrous hydrazine (0.03 mL) was added via argon-purged syringe. However,

methanol alone turned out to be enough to reduce the polymer as noted by the red color

transition occurring at the precipitation step. The reaction mixture was left to stir at room

temperature under argon for another 24 hours and then precipitated and collected as

described above. A yield of 0.0218 g (10.7%) of polymer was obtained as a dark red

powder.

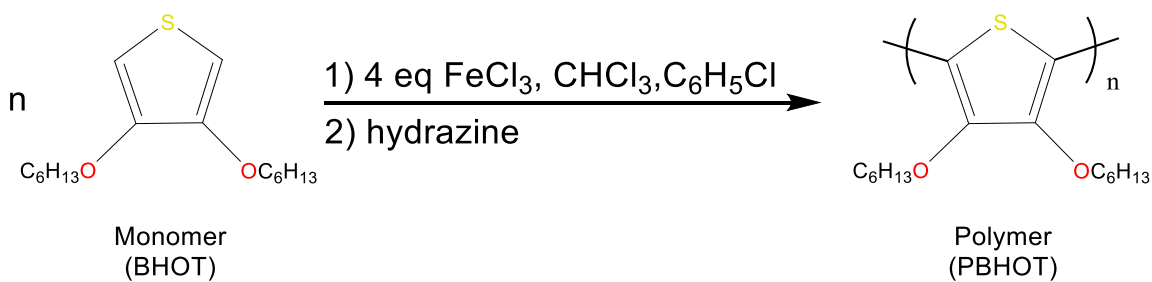*PBHOT – Standard Addition, 4 eq. FeCl$_3$ (48 hours)*

Scheme 7: Polymer synthesis of poly(3,4-bis(hexyloxy)thiophene) via chemical oxidation
of 3,4-bis(hexyloxy)thiophene.

The standard addition chemical oxidative polymerization of BHOT was

synthesized by Venus Stanton as follows. A Schlenk flask was fitted with a gas adaptor

connected to a bubbler and a magnetic stir bar was added. The Schlenk flask was dried in

an oven over night to remove as much moisture as possible before attempting the

reaction. BHOT (0.25109 g, 0.88 mmol) was added against positive argon flow to the

reaction flask and chlorobenzene (30 mL) was added via syringe with stirring. FeCl$_3$

(0.5726 g, 3.53 mmol) was quickly added to a vial and capped. Acetonitrile (5 mL) was

added via syringe through the septum cap to the FeCl$_3$ and the solution immediately

darkened. The solution was added dropwise via syringe to the reaction flask and was left

to stir at room temperature under argon for 48 hours. The polymer was then precipitated

and collected using the same method described above in the P3HT – Standard Addition,

2.3 eq. FeCl$_3$ protocol. The oxidized polymer was resuspended in chlorobenzene (40 mL)

and anhydrous hydrazine (0.0283 g, 0.88 mmol) was added to the reaction flask via

syringe through the septum cap. The reaction was left to stir at room temperature under

argon for 48 hours. The polymer was precipitated and isolated using the same method

described above. A yield of 38.9 mg (15.49%) of PBHOT was obtained as a dark purple

solid.

PBHOT – Grignard Metathesis
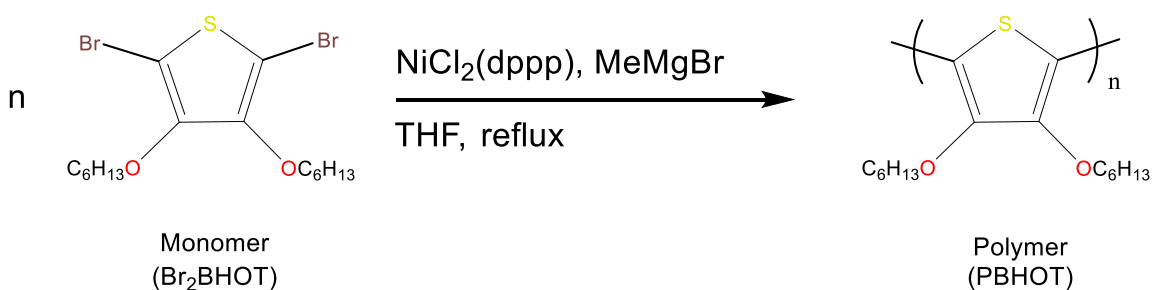
Scheme 8: Polymer synthesis of poly(3,4-bis(hexyloxy)thiophene) via Grignard metathesis of 3,4-bis(hexyloxy)thiophene.

A three-neck round bottom flask was outfitted with a condenser connected to an

argon bubbler. The other two necks were fitted with two septum caps and a magnetic stir

bar was added. The flask was placed in an oil bath and a thermocouple was used. The

three-neck round bottom flask will be referred as the reaction flask in this protocol. A

Schlenk flask was used as well to transfer contents from it into the reaction flask via

argon purged syringe. The apparatus pieces were dried in an oven over night to remove as

much moisture as possible before attempting the reaction and the apparatus was

assembled next to oven before moving to hood. Br$_2$BHOT (0.236 g, 0.534 mmol) was

added to a 50 mL Schlenk flask and NiCl$_2$(dppp) (0.00476 g, 7.738 µmol) was added to
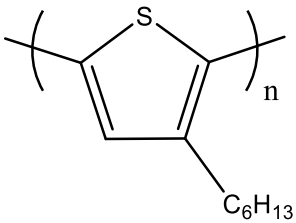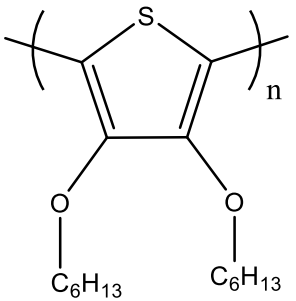
the reaction flask. The reaction flask and Schlenk flask was left under vacuum overnight. Dry THF (2.67 mL) was added to Schlenk flask via argon-purged syringe through the septum cap. Methylmagnesium bromide (0.266 mL, 3 M in Et_2O) was added via syringe to Schlenk flask and allowed to stir at room temperature for 65 minutes. Heat was turned up to 50 °C under reaction flask. Metalated monomer solution was transferred to the reaction flask via argon-purged syringe. Heat was turned up to 76 °C, condenser turned on, and stirring initiated. The reaction was then left to run overnight under argon at 76 °C with stirring. The temperature was brought down to 30 °C. The polymer was precipitated by adding the reaction mixture dropwise to stirred methanol (100 mL). The polymer was vacuum filtered through paper in a Büchner funnel and collected. Polymer was left in desiccator under high vacuum overnight. A yield of 96.21 mg (40.77%) polymer was obtained as a mahogany red solid.

Chemical Oxidative Polymerization

For each of the monomers that were tested (3HT and BHOT), the molecular weight of the polymer seemed to be dependent on the whether the reagents were added through reverse addition or standard addition (Table 1).[6] The GPC chromatograms for the ether-substituted polythiophene PBHOT and polyhexylthiophene P3HT can be found in Figures 3 and 4. Please note that the column used in the GPC has a 400,000 Da exclusion limit, meaning that values above 400,000 Da are approximate only.

Table 1. The following lists the weight-average molecular weight M_w, weight-average degree of polymerization X_w, and the yield for the polymers that were synthesized through $FeCl_3$-induced chemical oxidative polymerization under various parameters. The M_w was found and elucidated from the right-angle light scattering detector peak retention volume values. Entry 6 was not characterized due to being highly soluble in methanol (nonsolvent for polymers of this type) thus indicating it was an oligomer with very low molecular weight and not a polymer.

Polymer	Entry	Addition	Oxidant	Solvent	M_w	X_w	Yield
P3HT	1	Reverse	2.3 eq. (24 h)	C_6H_5Cl	37,000	222	64.4%
	2	Standard	2.3 eq. (24 h)	C_6H_5Cl	505,000	3,035	43.6%
	3	Standard	4 eq. (24 h)	C_6H_5Cl	4,110,000	24,716	24.8%
	4	Standard	4 eq. (48 h)	C_6H_5Cl	4,658,000	28,010	19.7%
PBHOT	5	Reverse	2.3 eq. (24 h)	C_6H_5Cl	4,500	16	42.3%
	6*	Standard	2.3 eq. (24 h)	C_6H_5Cl	N/A	N/A	78.1%
	7	Standard	4 eq. (24 h)	C_6H_5Cl	25,000	88	10.7%
	8	Standard	4 eq. (48 h)	C_6H_5Cl	3,000	11	15.5%

Between the two polymers, it was found that the 3,4-bis(hexyloxy)thiophene monomer BHOT was much less susceptible to significant molecular weight changes depending on the order of addition of the reagents. PBHOT was shown to only increase five-fold from 16 repeat units (4,500 g/mol) with the reverse addition reaction up to 88 repeat units (25,000 g/mol) with the standard addition reaction which was more-so significantly influenced by the increase of $FeCl_3$ equivalents from 2.3 to 4, respectively (Table 1, entry 5,7). This is in comparison to the P3HT reverse and standard addition reaction. The 3HT polymerizations showed an increase in molecular weight depending on the order of addition with a significant increase from 222 repeat units (37,000 g/mol) with the reverse addition reaction to 3,035 repeat units (505,000 g/mol) with the standard addition reaction (Table 1, entry 1, 2). Both reactions held all other parameters constant with only the order of addition varying, for P3HT.

It is believed that steric interactions among side-groups off the thiophene ring may contribute to limiting what molecular weights are achievable.[10] This interpretation had been drawn from the insignificant increase in molecular weight identified in PBHOT in comparison to the molecular weight of PEDOT-C_{12}, another polythiophene molecule that was synthesized in the Irvin Research Lab.
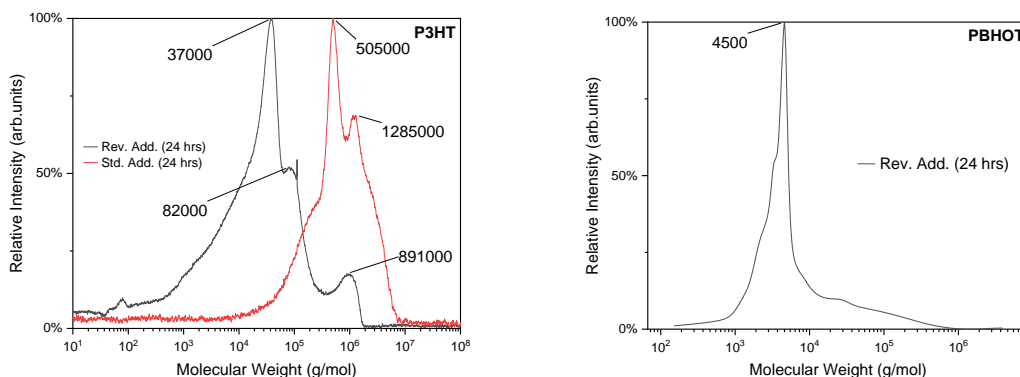
Figure 5: The GPC chromatograms for polyhexylthiophene and ether-substituted polythiophene PBHOT synthesized through 2.3 eq. FeCl$_3$-induced chemical oxidative polymerization. The black and red lines correspond to the polymers synthesized by the reverse and standard additions, respectively. Exclusion limit: 400,000 g/mol.

As illustrated in Figure 5 and Table 1 (entries 1,2,5), P3HT exhibited a significantly higher molecular weight achieved from both addition methods for 2.3 eq of FeCl$_3$ than PBHOT. The standard addition method for chemical oxidative polymerization of BHOT did not produce a polymer as indicated by its high solubility in methanol (nonsolvent for polymers of this type) which led to the determination that it was an oligomer with a very low molecular weight.[6]

After the standard addition method showed advantageous results, the equivalents parameter for FeCl$_3$ was adjusted to verify whether that would increase molecular weight as well. As indicated in Figure 6 and Table 1 (entries 3, 4, 7), there was a very significant increase in molecular weight when 4 equivalents of FeCl$_3$ were used instead of 2.3. 3HT polymerized with 2.3 equivalents using standard addition increased from 3,035 repeat units (505,000 g/mol) to 24,716 repeat units (4,110,000 g/mol) when polymerized with 4 equivalents. The molar ratio between FeCl$_3$ and 3HT has been indicated by another study to have influence over the yield and the molecular weight of the polymer.[11]
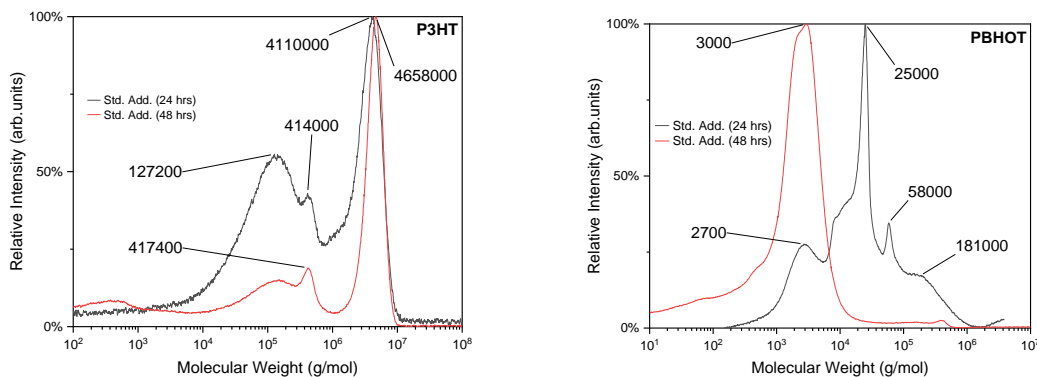

Figure 6: The GPC chromatograms for polyhexylthiophene and ether-substituted

polythiophene PBHOT synthesized through 4 eq. FeCl$_3$-induced chemical oxidative polymerization. The black and red lines correspond to the polymers synthesized by the 24 hour standard and 48 hour standard additions, respectively. Exclusion limit: 400,000 g/mol.

The P3HT formed under standard addition conditions for 24 hours at 4 equivalents did reveal a higher polydispersity index with a wide distribution of the molecular weight within the polymer, in comparison to the 48 hour P3HT condition with 4 equivalents. When BHOT was polymerized with 4 equivalents using standard addition, an increase was found from 16 repeat units (4,500 g/mol) with the reverse addition and 2.3 equivalents to 88 repeat units (25,000 g/mol), as further illustrated in Figure 6 and Table 1 (entries 5,7).

Time was another parameter optimized for the chemical oxidative polymerization of 3HT and BHOT. Equivalents of FeCl$_3$ was held constant at 4 and order of addition was kept as standard, with only the time for the oxidation and reduction steps both changing from 24 to 48 hours. As illustrated in Figure 6 and Table 1 (entries 3,4) the increase in time did result in an increase from 24,716 repeat units (4,110,000 g/mol) from the 24 hour condition to 28,010 repeat units (4,658,000 g/mol) with the 48 hour condition. Compared to the other parameter optimizations for P3HT, this was not as significant of a change in molecular weight, however the polydispersity index did seem to seem to decrease to a more uniform molecular weight distribution. As for PBHOT, the time optimization did not result in an increase but rather a decrease from 88 repeat units (25,000 g/mol) with the 24 hour condition to 11 repeat units (3,000 g/mol) with the 48 hour condition (Figure 6, Table 1, entry 7,8). However, the polydispersity of the polymer sample did seem to narrow to a more uniform molecular weight distribution. The

polydispersity improved at the expense of molecular weight, resulting in a very low

molecular weight, which was not ideal for this polythiophene.

The yield for both polymers synthesized varied depending on the parameter

adjusted. For P3HT, the yield was found to decrease while the degree of polymerization

increased when the order of addition was switched from reverse to standard. When

standard addition was used, there were more methanol-soluble oligomers present in the

filtrate post-oxidation after the polymers were precipitated into methanol and isolated,

which could partially account for the lower yields present from the polymers prepared

through standard conditions.[6] The yield of P3HT seemed to decrease with each parameter

adjustment when switched from 2.3 equivalents of $FeCl_3$ to 4 equivalents and even

further when switched from 24 hours to 48 hours. However, degree of polymerization

increased as well, at the expense of yield. For PBHOT, the yield may have been reported

as higher for the standard 2.3 equivalent condition, however no polymer was synthesized

due to the product being highly soluble in methanol (nonsolvent for this type of polymer)

indicating it was an oligomer with a very low molecular weight and thus not

characterized. However, when the order of addition was switched from reverse and 2.3

equivalents of $FeCl_3$ to standard and 4 equivalents, the yield remarkably decreased while

the degree of polymerization had a substantial increase. Adjusting the time of the

oxidation and reduction steps to 48 hours from 24 hours resulted in a slight increase in

yield of PBHOT, at the expense of much lower degree of polymerization (Table 1).

Grignard Metathesis Polymerization

The GPC chromatograms of P3HT and PBHOT can be found in Figure 7. Due to

the promising results produced from the Grignard Metathesis polymerization of ether-

substituted PEDOT-C$_{12}$ by David Hebert, it was suspected that ether-substituted PBHOT

would fare a significant increase in molecular weight in comparison to P3HT prepared

the same way.[6] However, as illustrated in Figure 7, BHOT polymerized through Grignard

Metathesis produced a very low degree of polymerization of 4 repeat units (1,100 g/mol)

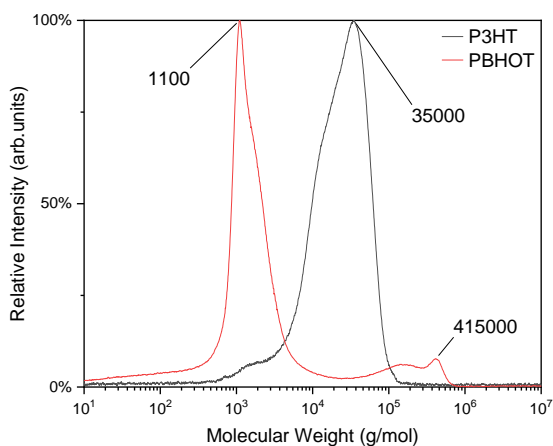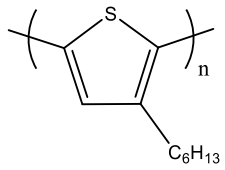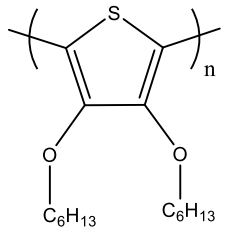in comparison to 210 repeat units (35,000 g/mol) for P3HT prepared the same way.

Figure 7: The GPC chromatograms for polyhexylthiophene and ether-substituted
polythiophene PBHOT synthesized through Grignard Metathesis. The black and red lines
correspond to P3HT and PBHOT, respectively. Exclusion limit: 70,000 g/mol (P3HT,
black line) and 400,000 g/mol (PBHOT, red line).

The PBHOT GPC chromatogram did show some molecular weight distribution

with a peak found in the 415,000 g/mol range. From this finding, it is possible that some

of the shorter polymers had yet to couple with each other and if allowed to grow to the

solubility limit, the sample could result in lower polydispersity and more uniform

molecular weight. From reports on PEDOT-C$_{12}$ synthesized through Grignard

Metathesis, monomer purity and dry solvent were critical factors in contributing to a high

molecular weight.[6] The PBHOT synthesized could have had impurities still present in the

BHOT monomer that influenced the very low molecular weight produced.

Comparison of Methods

Table 2. The following lists the weight-average molecular weight M_w, weight-average degree of polymerization X_w, and the yield for the best case polymers that were synthesized through $FeCl_3$-induced chemical oxidative polymerization and the polymers synthesized through Grignard Metathesis.

Polymer	Entry	Addition	Oxidant	Solvent	M_w	X_w	Yield
P3HT	1	Standard	4 eq. (24 h)	C_6H_5Cl	4,110,000	24,716	24.8%
	2	GRIM	N/A	THF	35,000	210	53.0%
PBHOT	3	Standard	4 eq. (24 h)	C_6H_5Cl	25,000	88	10.7%
	4	GRIM	N/A	THF	1,100	4	40.8%

Comparing the chemical oxidative polymerization (COP) and Grignard Metathesis (GRIM) methods for PBHOT, the data found that COP was better equipped to produce a polymer with a higher degree of polymerization (Figures 6,7). In addition, it was indicated that the sample characterized for the GRIM method was a tetramer and not a fully grown polymer, which could be the result of impurities still present in the monomer used. As for P3HT, COP and GRIM were both capable of producing substantial degrees of polymerization, however COP was better equipped to produce notably higher degrees of polymerization (Table 1, Figure 5,6,7). It is worth noting that for both P3HT and PBHOT, the adjustment in the time parameter from 24 hours to 48 hours for the oxidation/reduction steps resulted in the GPC chromatogram displaying a lower polydispersity illustrated in the curve (Figure 6). This is indicative of a more

uniform molecular weight distribution, however this was at the expense of a lower yield for P3HT and lower degree of polymerization for PBHOT.[12]

<div align="center">Conclusions</div>

Monomer Synthesis

By using an acid-catalyzed transetherification reaction, BHOT was synthesized in order to identify the impact of various reaction conditions on the molecular weight and yield of ether-substituted polythiophenes prepared through chemical oxidative polymerization. Commercially available 3HT was used for comparative purposes and to understand the impact of the various reaction conditions as well for chemical oxidative polymerization. The structure of BHOT was verified through ^{1}H NMR spectroscopy.

To further compare PBHOT and P3HT through a non-oxidative method, electrophilic aromatic substitution with two equivalents of *N*-Bromosuccinimide was used to synthesize the dibromo derivative of BHOT, Br$_2$BHOT. The dibromo derivative of 3HT, 2,5-dibromo-3-hexylthiophene, was commercially available and used for the Grignard Metathesis polymerization. The structure of Br$_2$BHOT was verified though ^{1}H NMR spectroscopy.

Polymerizations

The commonly used procedure (reverse addition) produced lower molecular weights and degree of polymerization for the ether-substituted polythiophene BHOT synthesized through chemical oxidative polymerization in comparison to the baseline standard, P3HT.[6] The lower degree of polymerization from the reverse addition method could be attributed to the lower oxidation potential of PBHOT compared to P3HT, making it more vulnerable to overoxidation when strongly oxidizing conditions are used.

Optimizing the order of addition to standard addition resulted in a notable increase in the

molecular weights and degrees of polymerization for both P3HT and PBHOT, at the

expense of lower yields obtained. However, switching from reverse to standard addition

did not result in a polymer for PBHOT at 2.3 equivalents of $FeCl_3$, due to its high

solubility in methanol (nonsolvent for this type of polymer). It was necessary to increase

to 4 equivalents of $FeCl_3$ for the standard addition in order to obtain a polymer with a

reasonable molecular weight and degree of polymerization in comparison to the reverse

addition. When increasing the reaction time from 24 to 48 hours, an increase in molecular

weight and degree of polymerization was found for P3HT, but not for PBHOT. Instead,

there was a significant decrease for PBHOT. However, when both polymers were

subjected to the increased time parameters, their respective GPC chromatograms

displayed a lower polydispersity, which was indicative of a more uniform molecular

weight achieved for the sample.

PBHOT synthesized through the non-oxidative method of Grignard Metathesis

exhibited low molecular weight and degree of polymerization in comparison to P3HT,

which could be attributed to the monomer, Br_2BHOT, not being purified enough or,

perhaps, to interactions between the ether substituents of the monomer with the transition

metal catalyst used in the reaction.

The oxidative method of chemical oxidative polymerization was shown to be

more reliable in comparison to the non-oxidative method of Grignard Metathesis for both

polymers. However, the susceptibility of the polymer to overoxidation is a critical factor

to consider.[6] For P3HT, various reaction parameters could be adjusted to achieve higher

molecular weights and degrees of polymerization through chemical oxidative

polymerization. For ether-substituted polythiophene PBHOT, reaction parameters had to be significantly adjusted to obtain higher molecular weights and degrees of polymerization, with each of these values still considerably low. Minimal optimization was suspected to be needed for the Grignard Metathesis polymerization of BHOT to achieve similar results, however as mentioned previously the purity of the monomer significantly dictates what molecular weights are achievable. These integral factors are critical components of the experimental design to consider for the synthesis of high molecular weight electron-rich thiophene based polymers.
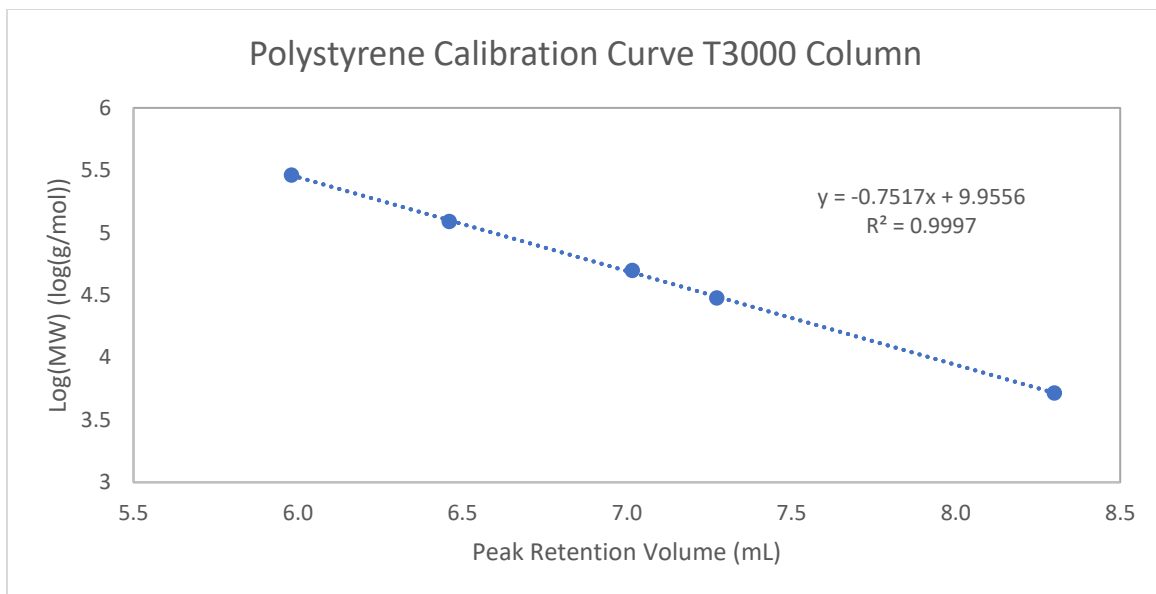
Appendix

Figure A1. Polystyrene calibration curve for the T3000 column for Fall 2020 (right-angle light scattering detector).
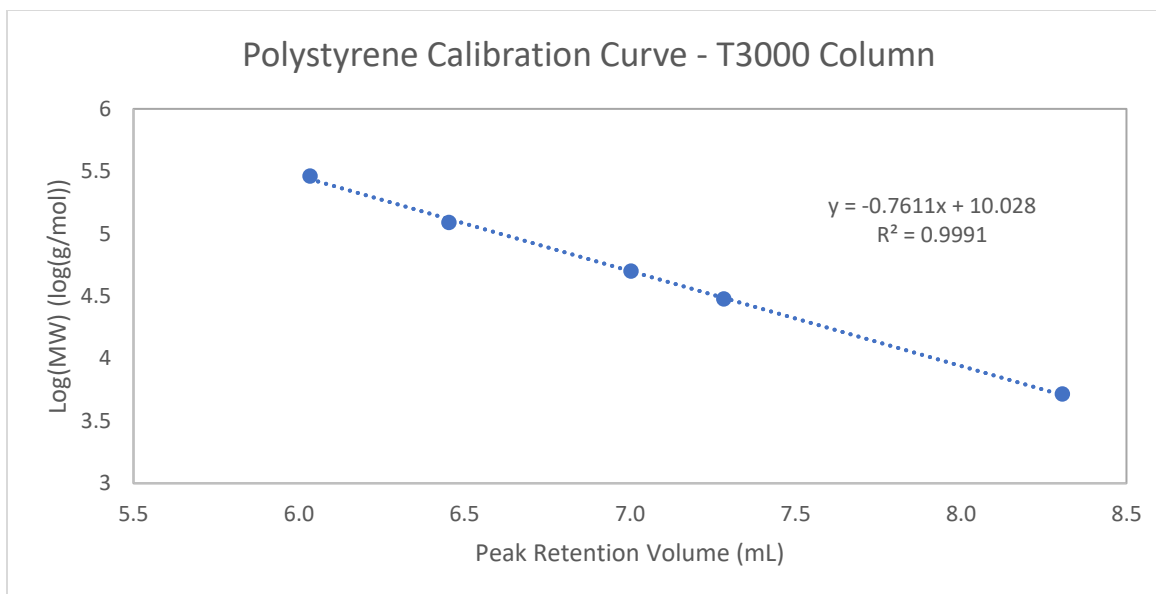

Figure A2. Polystyrene calibration curve for the T3000 column for Spring 2021 (right-angle light scattering detector).

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