Synthesis of poly(3-[2-{2-methoxyethoxy}ethoxy]thiophene) for Mixed Ionic Electronic Conductors

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Abstract

Synthesis of poly(3-[2-{2-methoxyethoxy}ethoxy]thiophene) for Mixed Ionic Electronic Conductors

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Material Science and Engineering

Mixed ionic-electronic conductors (MIECs) show great promise for applications ranging from biosensors and organic electrochemical transistors to fuel cells and batteries. However, there is still not much known about what makes a good MIEC. In this thesis, the syntheses of two ethylene glycol substituted thiophenes are presented to be studied as a MIEC. The synthesis starts with simple substituted thiophene rings and ends with dihalogented thiophene rings with ethylene glycol side chain. These monomers can then be polymerized to make poly(3-[2-{2-methoxyethoxy}ethoxy]thiophene) and poly(3-[2-{2-methoxyethoxy}ethoxymethyl]thiophene). The objective of this work is to help determine what constitutes a good MIEC.

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1. Introduction

In 1977, Heeger et al. reported the first electrically conductive polymer, polyacetylene, which was doped with arsenic pentafluoride. This polymer had a conductivity of 10^3 S cm^{-1}, which was an improvement of seven orders of magnitude over that of the undoped polymer.[1] This laid the foundation for the control of the conductivity of semiconducting polymers *via* molecular doping.[2]

One of the more studied conducting polymers is poly(3-hexylthiophene) (P3HT) due to its optoelectronic properties. P3HT has had reported mobility values of 3.1 cm^2 V^{-1} s^{-1} which is comparable to that of inorganic semiconductors.[3] The mobility of P3HT is dependent on the delocalization of the π-electrons along the backbone of the carbon chain. This occurs from the p_z orbital of the sp^2 hybridization of the carbon atoms. In P3HT, the one electron from carbon that is not a part of the σ bonds, forms a π-bond using the p_z orbital. These overlapping π electrons can form a π-band. The delocalized orbitals are only half filled so there exists a gap between the lowest unoccupied molecular orbital (LUMO) and the highest occupied molecular orbital (HOMO) which constitutes the band gap of semiconducting polymers.[2] The alkyl side chain of the thiophene ring can be varied in length in order to tune the physical properties of the polymer, such as solubility. Thiophene based polymers with alkyl side chains longer than butyl are found to be soluble whereas side chains that are shorter than butyl are found to be insoluble.[4] Another important part of mobility in P3HT is the regioregularity of the polymer. This is determined by the percentage of the head-to-tail attachment of the side chain on the 3 position of the thiophene ring. The higher the regioregularity the better the electrical conductivity as well as higher mobility.[2]

Since this first advancement in conjugated polymers in 1977, there have been many new polymers that have been developed for a wide range of applications. A subset of semiconducting polymers called mixed ionic electronic conductors (MIECs) are materials that show capacity for conducting ions in addition to electrons. These types of materials shows promise for applications in biosensors,[5] batteries and supercapacitors,[6] electrochemical windows[7] and in electrochemical transistors.[8] However, the morphology and conduction mechanisms of these materials are not well understood, hindering rational design of materials.[9]

Currently, there are two distinct classes of MIECs: conjugated polymers and ceramics which are both illustrated in figure 1. Ceramic materials exhibit good ionic conductivity but lack the electronic conductivity that is generated by conjugated polymers.[6] One advantage of the conjugated polymers is that they are generally easier to process than ceramics, which makes them better for scale up when it comes to mass production.[10]

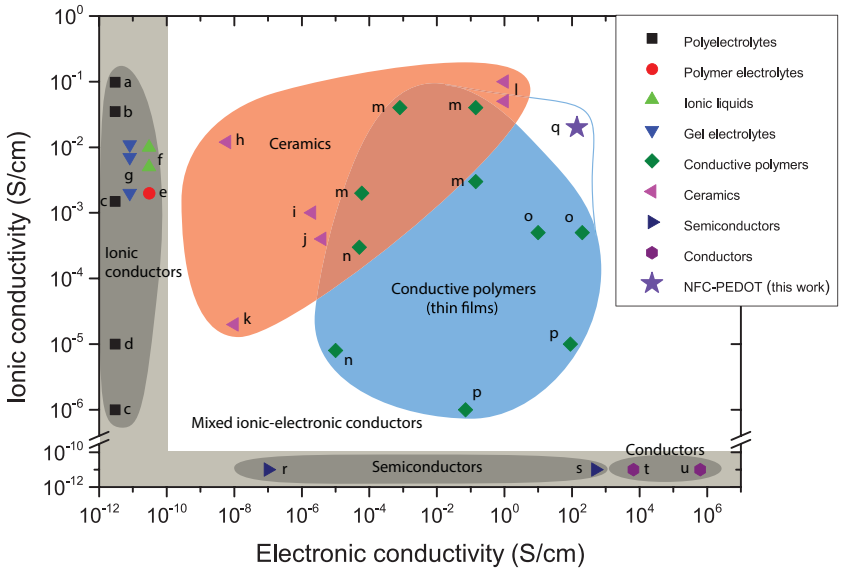


Figure 1. Comparison of Electronic and ionic conductors.[6]

PEDOT:PSS is the most commonly studied MIEC polymer because of its high ionic

conductivity. There are several studies that focus on PEDOT:PSS and how to change the properties of the polymer for certain applications.[6,8,9] Malti *et al*. reports that PEDOT:PSS can be optimized towards ionic conductors or semiconductors for applications such as fuel cells and batteries to transistors and sensors.[6]

MIECs also have the potential for organic electrochemical transistor (OECT). In these devices, the conducting polymer is deposited between a source and a drain electrode. This is then placed in direct contact with an electrolyte that has an Ag/AgCl gate electrode. When a bias is applied to the gate, ions move from the electrolyte into the bulk of the polymer film. This results in a change in the hole density, as well as the current that is flowing through the polymer. This means that OECTs are effective ion-to-electron transducers.[8]

In order to investigate the fundamental question of what makes good MIEC polymers, we investigated a new polymer system, shown in Figure 2. The polymer is made up of two monomers which consist of 3-octylthiophene and the second block is made up of 3-[2-{2-methoxyethoxy}ethoxy]thiophene. The rationale behind this is that poly(3-hexylthiophene) (P3HT) is a known semiconductor. We chose to use 3-octylthiophene however so that the side chains would be relatively the same length.

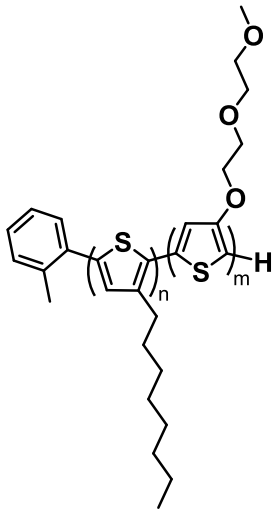


Figure 2. Proposed polymer system for mixed ionic electronic conductivity.

The rationale behind the substitution of the alkyl side chain for side chain containing poly(ethylene glycol) [PEG] is that PEG is known to have high ionic conductivity, particularly for lithium.[11] The ions are transported by the PEG *via* the formation and breakage of lithium-oxygen bonds. There are two mechanisms by which this motion can occur: intrachain or interchain hopping.[11] These mechanisms are shown in Figure 3. The proposed polymer is designed such that ion transport would occur exclusively through interchain hopping due to the short length of the PEG side chain. The rationale behind the substitution of the alkyl side chain for an ethylene glycol chain is that poly(ethylene glycol) is known to be a good ionic conductor.[11] There has been extensive studies on the properties of poly(ethylene glycol) and how to improve its ionic conductivity for lithium ion batteries.[12, 13] The ions are able to move through the electrolyte by the formation and breaking of lithium oxygen bonds. There are two mechanisms in which the ion can move, either by intrachain or interchain hopping.[11] These mechanisms are shown in Figure 3. Because of the way that our polymers are designed, the side chain is short enough to prohibit

intrachain hopping, so the ion transport would have to occur through interchain hopping.

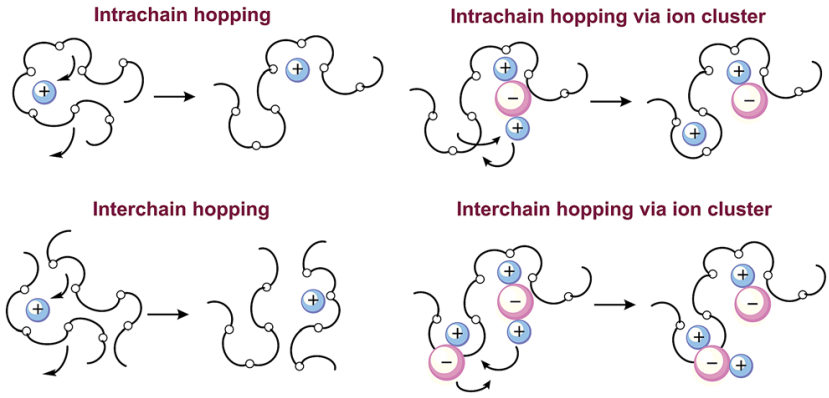


Figure 3. Mechanism of how ions move in PEG.[11]

The goal of this project is to make eight polymers, two of which will be homopolymers of the poly(3-octylthiophene) and the other will be poly(3-[2-{2-methoxyethoxy}ethoxy]thiophene). We will then make random copolymers and block copolymers of varying composition in order to help understand the phase behavior, as well as the transport properties of these materials.

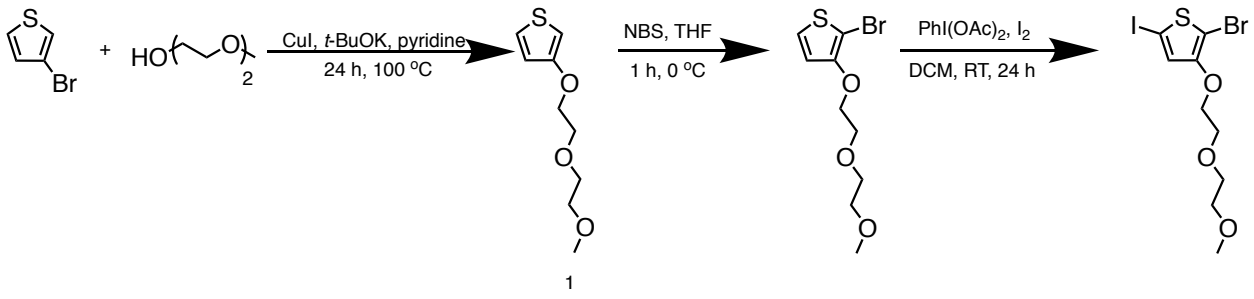
2. Experimental

2.1 Materials and Instrumentation

N-bromosuccinimide (NBS, Oakridge Chemical) was recrystallized from deionized water before use. Tetrahydrofuran (THF) was dried using a drying system from Innovative Technologies. The diethylene glycol methyl ether (Sigma-Aldrich) was dried with sodium sulfate. All Grignard reagents (Sigma-Aldrich) were titrated using the I_2/LiCl method. All other materials were used as purchased (Sigma-Aldrich). ^{1}H NMR spectra were obtained on a Bruker AV-500 or a Bruker AV-300 using $CDCl_3$ (Cambridge Isotope Laboratories) as a solvent. MALDI spectra were recorded on

a Bruker Autoflex II spectrometer. Grignard conversion ratios were check by quenching Grignardized monomer in methanol.

2.2 Synthetic Route 1



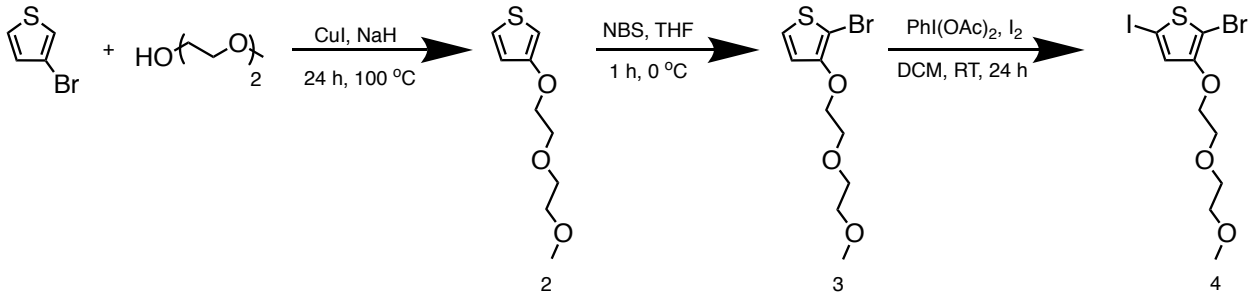
Scheme 1. Synthetic route for 3-[2-(2-methoxyethoxy)ethoxy]thiophene.

3-[2-(2-methoxyethoxy)ethoxy]thiophene (1)

Compound 1 was prepared following a modified synthesis from Xue et al.[14] Copper(I) iodide (399 mg, 2.1×10^{-3} mol), potassium tert-butoxide (1.69 g, 1.5×10^{-2} mol), and diethylene glycol methyl ether (6.3 mL, 5.4×10^{-2} mol) were added to a 3-neck round bottom flask. The flask was then flushed with nitrogen gas and then 5 mL of pyridine was added to the flask. The solution was stirred for 30 minutes before adding 0.985 mL (1.05×10^{-2} mol) of 3-bromothiophene. The flask was then heated to 100 °C for 24 hours, and then allowed to cool to room temperature. Crude NMR showed about 1% conversion, so another 1.768 g (1.6×10^{-2} mol) of potassium tert-butoxide was added and allowed to react for 24 hours at 100 °C. The solution was filtered and washed with dichloromethane. Then the solution was washed with 10% hydrochloric acid, 10% ammonium chloride, and then with brine. The solvent was removed under reduced pressure. The crude product was then eluted over silica gel using a 50:50 solution of hexanes:ethyl acetate to

give a yellow oil (<5% yield).

2.3 Synthetic Route 2



Scheme 2. Synthetic route for 2-bromo-3-[2-(2-methoxyethoxy)ethoxy]thiophene.

3-[2-(2-methoxyethoxy)ethoxy]thiophene (2)

Compound 2 was prepared from a modified synthesis by Xue et al.[14] Copper(I) iodide (1.334 g, $7x10^{-3}$ mol), sodium hydride (2.106 g, $5.25x10^{-2}$ mol, 60% in mineral oil), and diethylene glycol monomethyl ether (20.5 mL, 0.175 mol) were added to a 3-neck round bottom flask. The flask was sealed under a nitrogen atmosphere once the hydrogen gas evolution ceased. The solution was stirred for thirty minutes before adding 3.3 mL ($3.5x10^{-2}$ mol) of 3-bromothiophene. The flask was then heated to 100 °C for 24 h, and then allowed to cool to room temperature. The solution was filtered and washed with dichloromethane. Then the solution was washed with 10% aqueous ammonium chloride followed by brine. The solvent was then removed under reduced pressure. The crude product was then eluted over silica gel using a 60:40 solution of hexanes:ethyl acetate to give a yellow oil (4.277 g, 60% yield). Spectral data: ^{1}H NMR (500 MHz, $CDCl_3$): δ_h 3.39 (s, 4H), 3.58 (m, 3H), 3.71 (m, 3H), 3.84 (m, 3H), 4.14 (m, 3H), 6.26 (dd, 1H), 6.78 (dd, 1H), 7.17 (dd, 1H)

2-bromo-3-[2-(2-methoxyethoxy)ethoxy]thiophene (3)

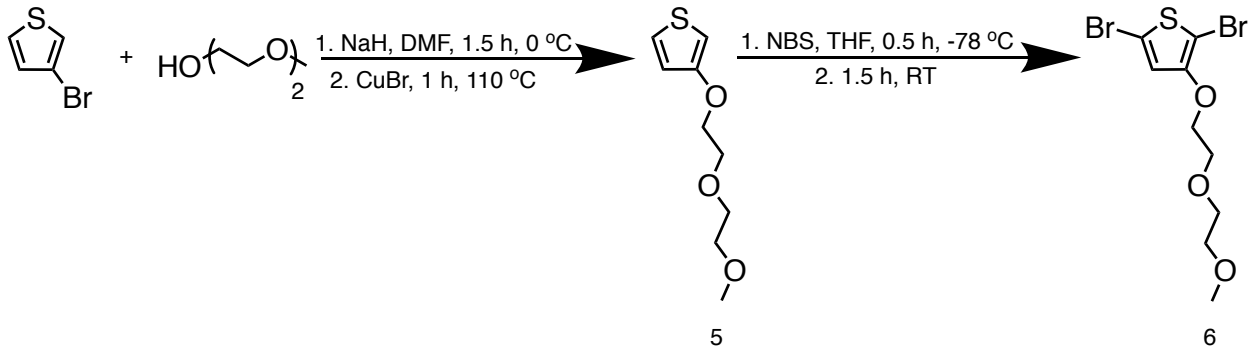
3-[2-(2-methoxyethoxy)ethoxy]thiophene (1.220 g, $6x10^{-3}$ mol) was dissolved in 30 mL of anhydrous THF and cooled to 0°C. NBS (1.063 g, $6x10^{-3}$ mol) was then added slowly and allowed to dissolve. The reaction was placed under a nitrogen atmosphere and stirred for one hour. The reaction was quenched in water and extracted with diethyl ether. The organic solution was dried with sodium sulfate and then the solvent was removed under reduced pressure. The product was a yellow liquid (1.234 g, 73% yield). Spectral data: ^{1}H NMR (300 MHz, $CDCl_3$): δ_h 3.39 (s, 3H), 3.57 (m, 2H), 3.73 (m, 2H), 3.83 (m, 2H), 4.21 (m, 2H, 6.77 (d, 1H), 7.17 (d, 1H)

2-bromo-5-iodo-3-[2-(2-methoxyethoxy)ethoxy]thiophene (4)

Compound 3 (1.222 g, $4.3x10^{-3}$ mol) was placed in a round bottom flask and then sealed under a nitrogen atmosphere. Anhydrous dichloromethane (40 mL) was added to the flask to dissolve compound 3. The flask was then placed in an ice bath at 0 °C. After allowing the flask to cool, iodine (560 mg, $2.2x10^{-3}$ mol) and (diacetoxyiodo)benzene (773 mg, $2.4x10^{-3}$ mol) was added to the flask. The flask was allowed to stir in the ice bath for one hour before removing from the ice bath, and continuing to stir at room temperature. After eight hours at RT, a crude NMR was taken to check conversion ratio. More iodine and (diacetoxyiodo)benzene was added according to conversion ratio. This addition followed the same procedure as above, where the flask was placed in an ice bath at 0 °C and allowed to stir for one hour in the ice bath. Once the reaction was run to completion, the residual iodine was extracted with 10% sodium thiosulfate washes. The solution was then washed with sodium bicarbonate, and then with brine. The organic solution was then dried with sodium sulfate and the solvent was removed under reduced

pressure. Finally, the product was eluted over a silica plug using hexanes to remove residual iodine.

2.4 Synthetic Route 3



Scheme 3. Synthetic route for 2,5-dibromo-3-[2-(2-methoxyethoxy)ethoxy]thiophene.

3-[2-(2-methoxyethoxy)ethoxy]thiophene (5)

Compound 5 was synthesized following the procedure by Sheina et al.[15] Sodium hydride (1.805 g, 4.5×10^{-2} mol, 60% in mineral oil) was added to a 3-neck round bottom flask along with 7.5 mL of dimethylformamide. The flask was equipped with an addition funnel and placed under nitrogen atmosphere. Next, the flask was placed in an ice bath at 0 °C. Diethylene glycol monomethyl ether (17 mL, 0.144 mol) was added to the addition funnel. The diethylene glycol monomethyl ether was added dropwise to the flask and allowed to stir for one hour. Copper (I) bromide (480 mg, 3×10^{-3} mol) and 3-bromothiophene (2.8 mL, 3×10^{-2} mol) were added to the flask. The reaction was then taken out of the ice bath and placed in an oil bath at 110 °C for two hours. After removing from the oil bath, the reaction was quenched with 50 mL of 1 M ammonium chloride and allowed to stir for ten minutes. The product was extracted with hexanes

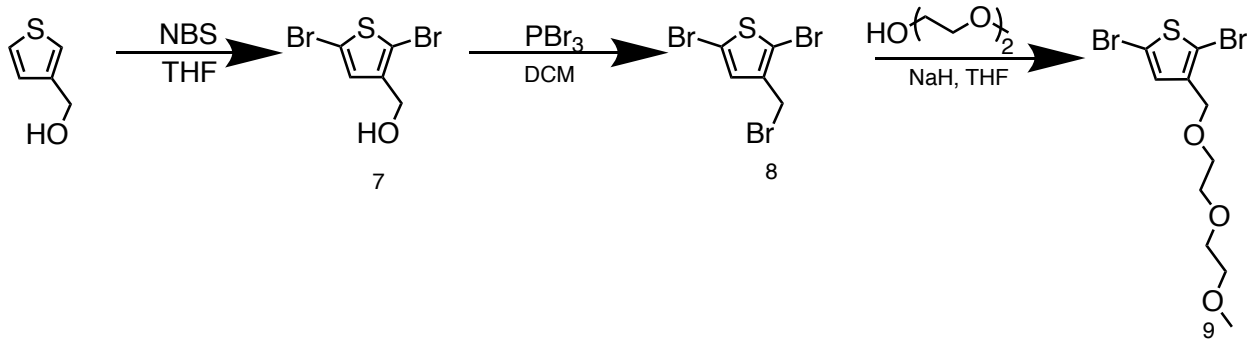
and dried with magnesium sulfate. The dried solution was filtered and the solvent was removed under reduced pressure yielding a yellow oil. The product was further purified *via* distillation at 140 °C at 0.62 torr.

2,5-dibromo-3-[2-(2-methoxyethoxy)ethoxy]thiophene (6)

Compound 6 was synthesized following the procedure by Sheina et al.[15] 3-[2-(2-methoxyethoxy)ethoxy]thiophene (2.492 g, $1.2x10^{-2}$ mol) was dissolved in 42 mL of THF in a round bottom flask. The flask was placed in a -78 °C bath and put under a nitrogen atmosphere. N-bromosuccinimide (4.805 g, $2.7x10^{-2}$ mol) was added and stirred for 30 minutes before the flask was removed from the ice bath. The reaction was stopped after two hours. The solvent was then removed under reduced pressure. The product was extracted with hexanes and filtered over Celite®. The solvent was then removed under reduced pressure. The product was purified by eluting over silica gel using a 90:10 mixture of hexanes:ethyl acetate. The product was then dried with magnesium sulfate and activated carbon to remove any radical species. The product was then filtered over Celite® and the solvent was removed under reduced pressure. The product was a yellow oil that was stored under a nitrogen atmosphere and in the freezer at -20 °C in a UV-Vial. Spectral data: ^{1}H NMR (300 MHz, $CDCl_3$): δ_h 3.39 (s, 4H), 3.56 (m, 3H), 3.71 (m, 3H), 3.80 (m, 3H), 4.17 (m, 3H), 6.82 (s, 1H)

2.5 Synthetic Route for 2,5-dibromo-3-[2-(2-methoxyethoxy)ethoxymethyl

]thiophene



Scheme 4. Synthetic route for 2,5-dibromo-3-[2-(2-methoxyethoxy)ethoxymethyl]thiophene.[16]

2,5-dibromo-3-thiophenemethanol (7)

Compound 7 was synthesized according to Lee et al.[16] 3-thiopehemethanol (0.36 mL, $3.8x10^{-3}$ mol) was dissolved in 4.5 mL of THF. N-bromosuccinimide (1.791 g, $1x10^{-2}$ mol) was added to the reaction slowly. The reaction was allowed to stir overnight while under a nitrogen atmosphere. The solution was then filtered over Celite® with THF and the solvent was removed under reduced pressure. Diethyl ether was used to extract the product which was then washed with 10% sodium hydroxide and then DI water. The product was then dried with sodium sulfate and the solvent was removed under reduced pressure. Column chromatography was used to purify the product using an 80:20 mixture of hexanes:ethyl acetate over silica gel. The product was a white solid (0.745 g, 54% yield). Spectral data: ^{1}H NMR (300 MHz, $CDCl_3$): δ_h 4.55 (s, 3H), 7.00 (s, 1H)

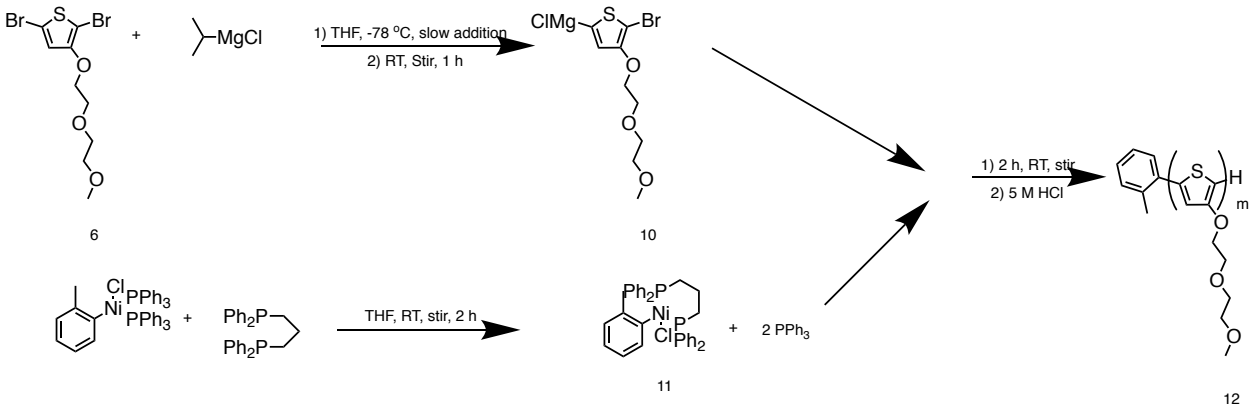
2,5-dibromo-3-bromomethylthiophene (8)

Compound 8 was synthesized according to Lee et al.[16] Compound 7 (0.745 g, $2.7x10^{-3}$ mol) was dissolved in anhydrous dichloromethane (15 mL) and placed under a nitrogen atmosphere. The solution was placed in an ice bath at 0 °C. Phosphorus tribromide (0.26 mL, $2.8x10^{-3}$ mol) was then added to the flask dropwise over 15 minutes. The reaction was then taken off the ice bath and allowed to react at room temperature for 5 h. Then the reaction was quenched with a 10% solution of sodium bicarbonate. The organic layer was extracted and run through a plug of Celite® with dichloromethane. The product was dried with magnesium sulfate and then filtered. Solvent was removed under reduced pressure. The product was a yellow solid (756 mg, 82% yield). Spectral data: ^{1}H NMR (300 MHz, $CDCl_3$): δ_h 4.36 (s, 3H), 6.99 (s, 1H)

2,5-dibromo-3-[2-(2-methoxyethoxy)ethoxymethyl]thiophene (9)

Compound 9 was synthesized according to Lee et al. with slight modifications.[16] Diethylene glycol methyl ether (0.27 mL, $2.32x10^{-3}$ mol) was dissolved in 9.75 mL of THF in a 3-neck round bottom flask equipped with an addition funnel. Sodium hydride (104 mg, $2.6x10^{-3}$ mol) was added to the flask. Once hydrogen gas evolution ceased, the flask was sealed under a nitrogen atmosphere. Compound 8 (756 mg, $2.3x10^{-3}$ mol) was dissolved in 1.9 mL of THF. This solution was added to the reaction slowly over the course of ten minutes *via* syringe. The reaction was stirred at room temperature for four hours. Then the reaction was filtered over Celite® using THF. The solvent was removed under reduced pressured and the product was purified using column chromatography with a 70:30 hexanes:ethyl acetate mixture over silica gel. Spectral data: ^{1}H NMR (500 MHz, $CDCl_3$): δ_h 3.34 (s, 3H), 3.51 (m, 2H), 3.59 (m, 6H), 4.39 (s, 2H), 6.96 (s, 1H)

2.6 Polymerization Synthesis



Scheme 5. Polymerization scheme for poly(3-[2-{2-methoxyethoxy}ethoxy]thiophene).

2-bromo-5-chloromagnesio-3-[2-(2-methoxyethoxy)ethoxy]thiophene (10)

Compound 6 (377 mg, $1x10^{-3}$ mol) was dried under vacuum for 30 minutes. THF (8mL) was added to the flask and then placed under a nitrogen atmosphere. The flask was placed in an dry ice/acetone bath at -78 °C and isopropylmagnesium chloride (0.61 mL, 1.55 M) was added dropwise over ten minutes. The reaction was stirred for one hour.

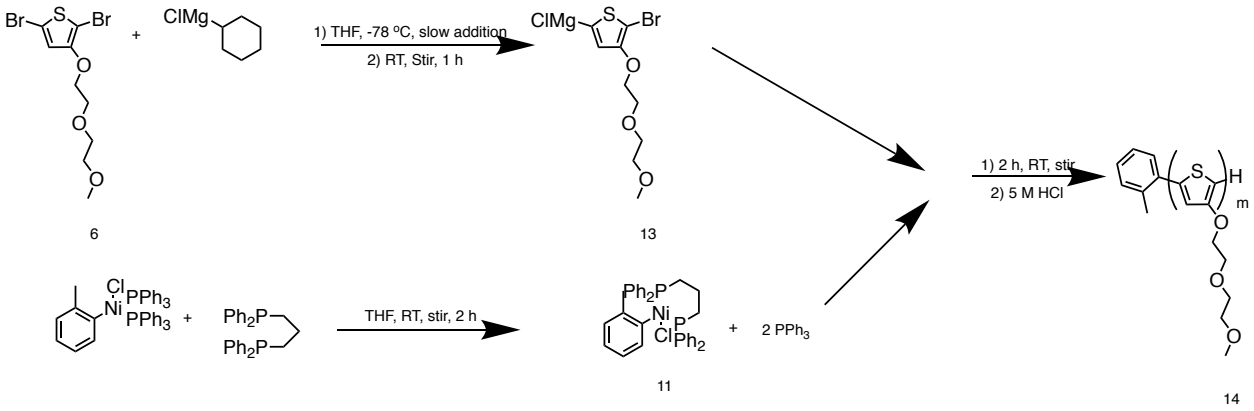
cis-chloro(*o*-tolyl)1,3-bis(diphenylphosphino)propane (11)

Compound 11 was synthesized according to Bronstein and Luscombe. [17] 1,3-bis(diphenylphosphino)propane (7.866 mg, $1.9x10^{-5}$ mol) and *trans*-chloro(*o*-tolyl)bis(triphenylphosphine)nickel(II) (7.207 mg, $9.5x10^{-6}$ mol) were added to a Schlenk flask and dried under vacuum. THF (1 mL) was added to the flask and the reaction was placed under a nitrogen atmosphere. The reaction was stirred for two hours.

Poly(3-[2-{2-methoxyethoxy}ethoxy]thiophene) (12)

Compound 12 was synthesized according to Bronstein and Luscombe.[17] Compound 11 was added to compound 10 and allowed to stir for two hours at room temperature under a nitrogen atmosphere. Then the polymerization was quenched with 1.1 mL of 5 M hydrochloric acid. After 30 minutes of stirring, the reaction was precipitated into hexane.

2.7 Revised Polymerization Synthesis



Scheme 6. Polymerization scheme for poly(3-[2-{2-methoxyethoxy}ethoxy]thiophene).

2-bromo-5-chloromagnesio-3-[2-(2-methoxyethoxy)ethoxy]thiophene (13)

Compound 6 (377 mg, $1x10^{-3}$ mol) was dried under vacuum for 30 minutes. THF (8mL) was added to the flask and then the flask was placed under a nitrogen atmosphere. The flask was placed in a dry ice/acetone bath at -78 °C and cyclohexylmagnesium chloride (0.60 mL, 1.55 M) was added dropwise over ten minutes. The reaction was stirred for one hour.

Poly(3-[2-{2-methoxyethoxy}ethoxy]thiophene) (14)

Compound 14 was synthesized according to Bronstein and Luscombe.[17] Compound 11 was added to compound 13 and allowed to stir for two hours at room temperature while under a nitrogen atmosphere. Then the polymerization was quenched with 1.1 mL of 5 M hydrochloric acid. After 30 minutes of stirring, the reaction was precipitated into hexane.

3. Results and Discussion

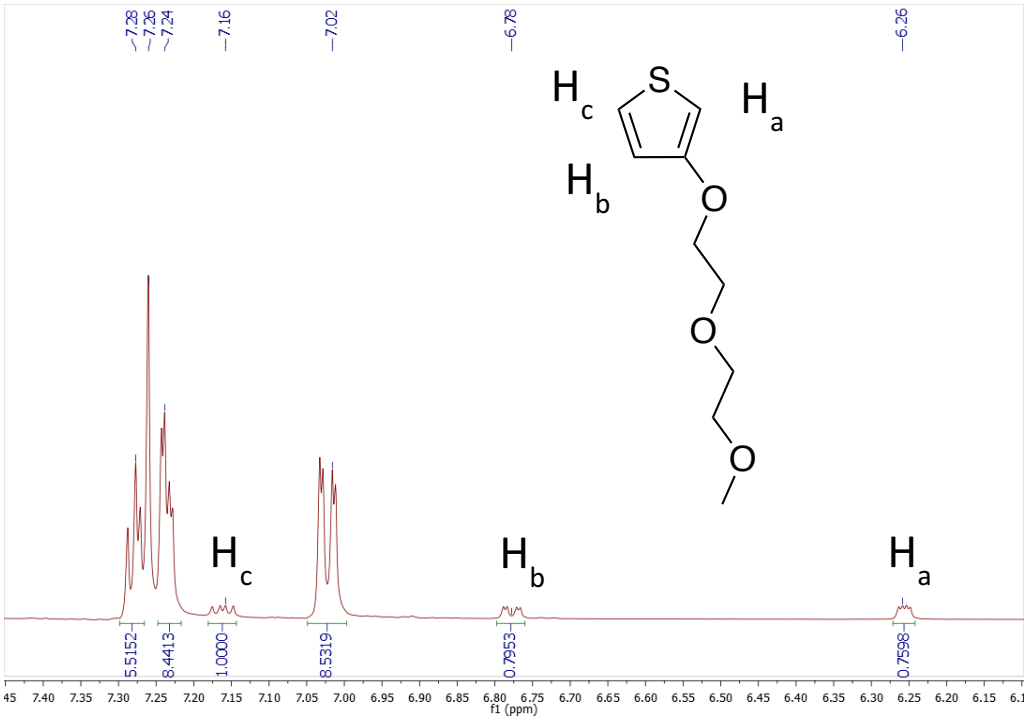


Figure 4. ^{1}H NMR of compound 1.

On our first attempt to synthesize 3-[2-(2-methoxyethoxy)ethoxy]thiophene yielded roughly an eight percent conversion that can be seen in Figure 4 by comparing the integration ratio of the product peaks at 7.05 ppm to the reactant peaks at 6.28 ppm. According to literature,

[14] a 75% yield was expected after purification. It was determined that the cause for low yield was due to water-based degradation of the potassium *t*-butoxide. Due to this, alternative bases were investigated that also could not participate in reactions with the bromine positions. Ultimately sodium hydride was selected according to a procedure by Sheina.[15] In addition, we tried the same procedure but with lithium *t*-butoxide based on Huang *et al*.[18] Based off of the crude NMR, sodium hydride had a conversion of 80% compared to lithium *t*-butoxide which had a conversion of 78%. We also removed the pyridine and ran the experiment with excess diethylene glycol methyl ether as the solvent based on the work of Huang et al.[18] This change in procedure resulted in a 60% yield and a clean NMR as shown in Figure 5.

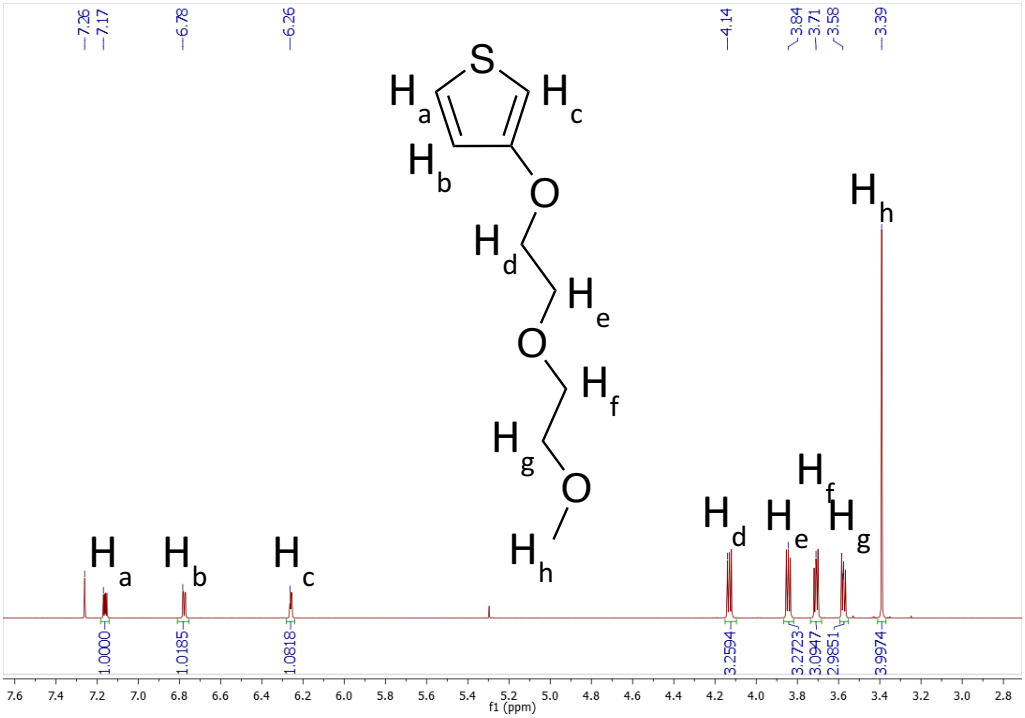


Figure 5. [1]H NMR of compound 2.

After synthesizing the ethylene glycol side chain modified thiophene ring, the next step

was to halogenate the thiophene ring. The halogen substitutions are needed to enable the polymerization mechanism and act as leaving groups during the polymerization. The ideal monomer would have an iodine in the 5 position on the thiophene ring and a bromine on the 2 position of the ring. This would lead to a higher conversion of the Grignard at the 5 position because the iodine would be more reactive, allowing for an improvement of regioregularity control.

Successful bromination of the 2 position was achieved, which can be seen in Figure 6 by the disappearance of the peaks at 6.26 ppm in Figure 5. However, upon halogenation of the thiophene ring, we began to have stability issues with the monomer, resulting in color changes, and debromination. These stability issues were also reported by Marsella *et al.* for 3-alkoxythiophenes. [7] We were never able to attach the iodine to the 5 position of this monomer. Based on these findings, the decision was made to make 2,5-dibromo-3-[2-(2-methoxyehtoxy)ethoxy]thiophene using NBS to minimize synthetic steps. Successful synthesis of this compound was determined; however, the compound was very unstable and underwent autopolymerization on several occasions. These autopolymerizations occurred under exposure to light and air, and were more common at room temperature than -20 °C. A potential possibility for this excessive reactivity is that there was residual copper that was chelated by the ethylene glycol side chain, and this copper catalyzed the autopolymerization. This hypothesis could be confirmed by running inductively coupled plasma atomic emission spectroscopy. Wu et al. also reports that poly(3-[2-{2-methoxyethoxy}ethoxy]thiophene) does in fact chelate copper ions.[19] With all of this information, we decided to change the procedure to follow scheme 3 based off of the procedure by Sheina et al. with the premise that distillation would allow for separation of

the 3-[2-(2-methoxyethoxy)ethoxy]thiophene from the copper.[15].[15]

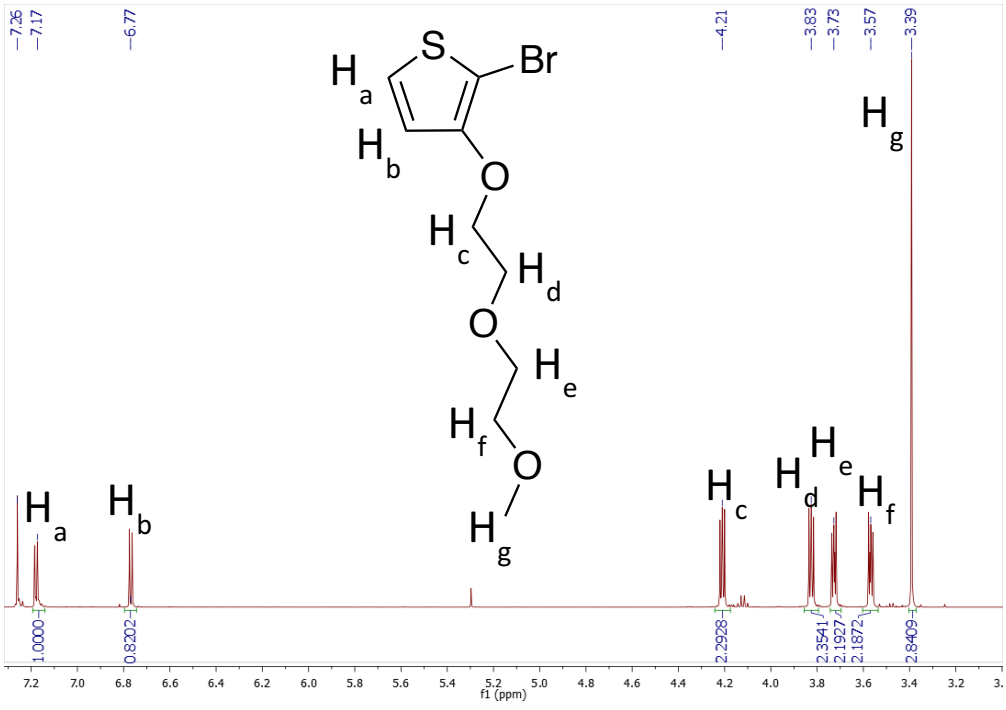


Figure 6. ^{1}H NMR of compound 3.

The synthesis of compound 5 resulted in a clean product. We were then able to take compound 5 and brominate the 2 and 5 positions. One unique purification step that was added following the procedure by Sheina et al.[15] is the addition of activated carbon when drying the product. The activated carbon removes residual radicals from the NBS bromination procedure that may lead to autopolymerization. It is important to note that compound 6 must be stored under nitrogen, in a dark place, and in the freezer to help keep the compound stable. When left in air and at room temperature, the compound changes from a yellow liquid to a faint red liquid. This color change can be reversed by filtering through activated carbon again. An NMR of the

final product of compound 6 is shown in Figure 7.

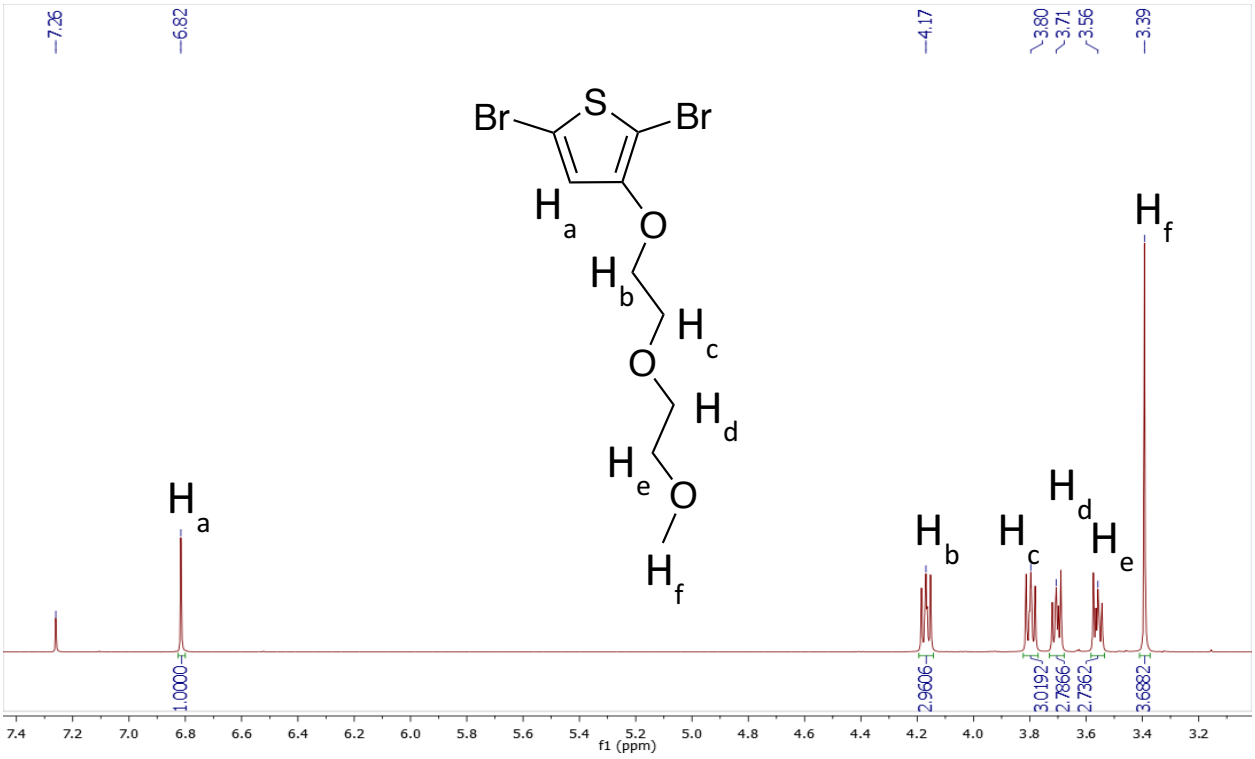


Figure 7. ^{1}H NMR of compound 6.

We then attempted to synthesize a new monomer shown in scheme 4. By adding a methyl spacer between the first oxygen in the ethylene glycol side chain and the thiophene ring, the stability might increase, due to a reduction in the donating effect of the oxygen. An additional advantage to this synthesis is that the attachment of the ethylene glycol side chain is no longer an aromatic substitution, but an SN_2 reaction, simplifying the chemistry, and removing the need for a copper catalyst. The NMR of the purified compounds 7 and 8 are shown in Figure 8 and Figure 9, respectively. Confirmation of bromination of the 2 and 5 positions of the thiophene was observed by the presence of only one aromatic peak at 7.00 ppm in Figure 8. We also used gas chromatography mass spectroscopy which confirmed we made our product. It also showed that

we did make a small amount of tribominated product. This was due to an error made in the density of the 3-thiophene methanol, which lead to a larger excess in NBS. The shift in the peak at 4.55 ppm to 4.36 ppm in Figure 9 corresponds to the shift due to the increased shielding due to the bromine replacing the alcohol on the methyl group at the 3 position of the thiophene ring.

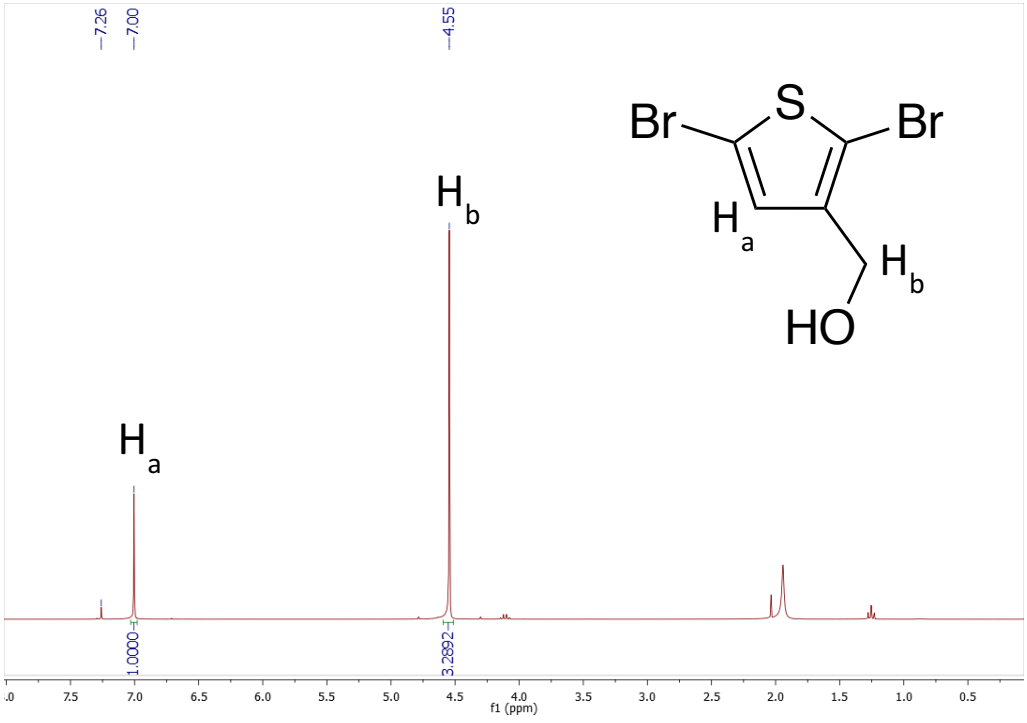


Figure 8. ^{1}H NMR of compound 7.

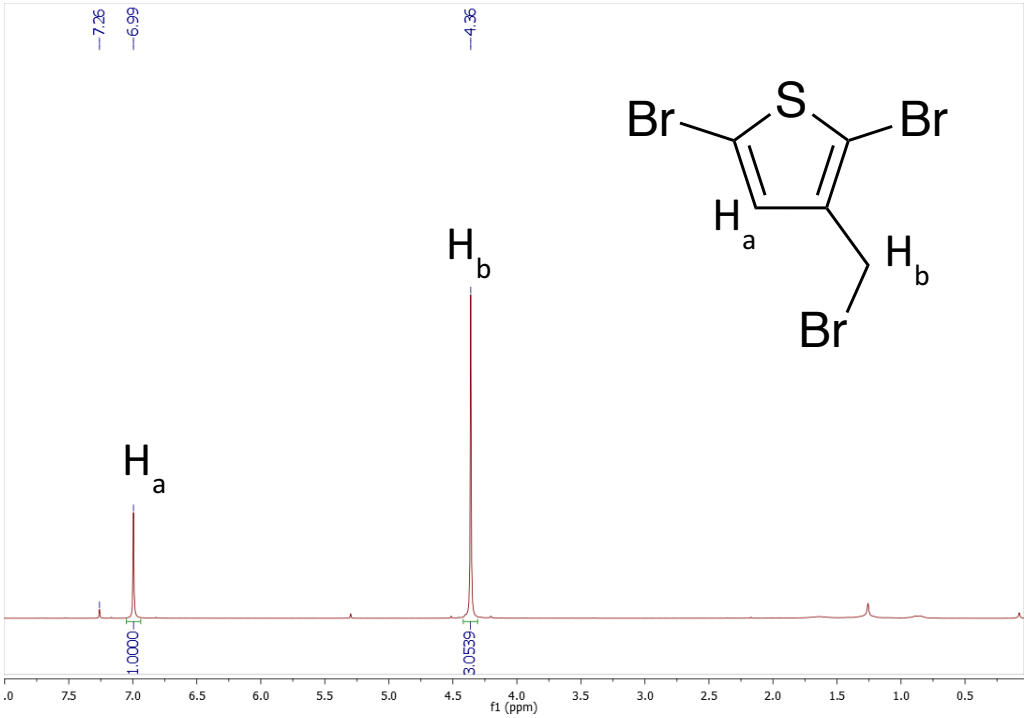


Figure 9. ^{1}H NMR of compound 8.

Figure 10 shows a clean NMR of compound 9. The column run to purify compound 9 yielded four different compounds. NMR shows the formation of either an aldehyde or of a carboxylic acid. Based on other peaks seen in the NMR, this aldehyde or carboxylic acid must have formed on the diethylene glycol methyl ether. We are not sure exactly how this could have formed, but more reactions with different reaction conditions may be able to eliminate the formation of these products.

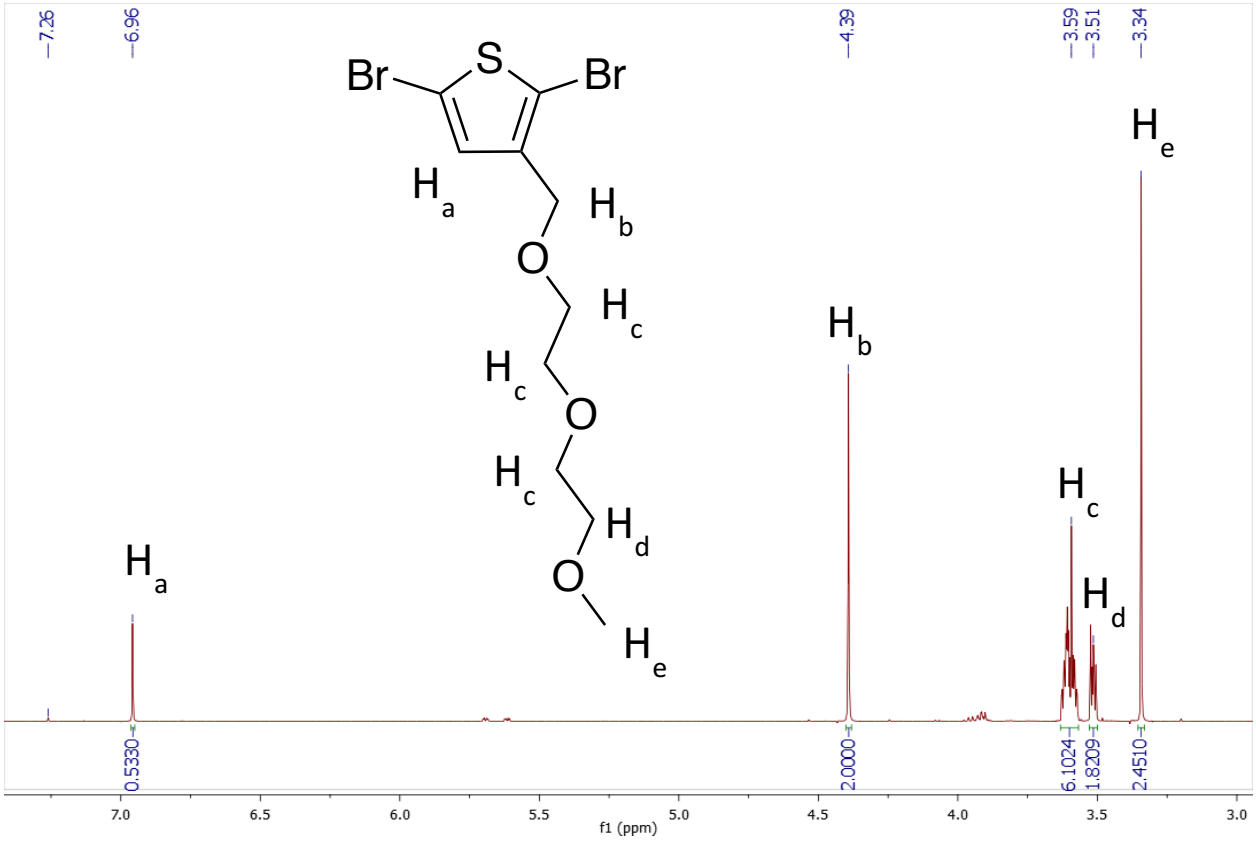


Figure 10. ^{1}H NMR of compound 9.

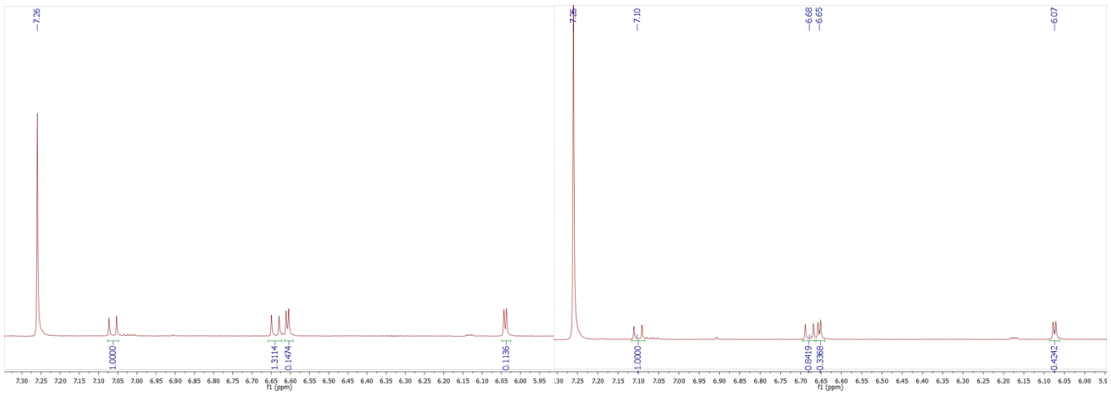


Figure 11. ^{1}H NMR of Grignard conversions of compound 10. On the left, the reaction was run in a -78 °C dry ice/acetone bath. On the right, the reaction was done in an ice bath at 0 °C.

When polymerizing, it is important to try and Grignardize the 5 position over the 2

position in order to obtain a regioregular polymer with minimal head to head coupling. Figure 11 shows the Grignard conversion at two different temperatures using isopropylmagnesium chloride as the Grignard reagent. The NMR spectra on the left was done by adding the isopropylmagnesium chloride while in a -78 °C dry ice/acetone bath. This resulted in a conversion of about 89% at the 5 position. The NMR spectra on the right is done when the isopropylmagnesium chloride is added while in an ice bath at 0 °C. This resulted in a conversion at the 5 position of about 70%, which would result in a polymer with only 70% regioregularity. In order to improve this, a bulkier Grignard reagent with more sterics could be used, which should improve directing of the Grignard to the less sterically hindered 5 position. Cyclohexylmagnesium chloride was selected as the bulkier Grignard as it is one of the most sterically hindered commercially available Grignard reagents.[15]

We have also run the polymerizations that are listed in scheme 4. So far though they have not yielded the correct degree of polymerization. We were shooting for a degree of polymerization of 100 but according to MALDI data, we have only reached a degree of polymerization of 17. This can be seen in figure 12.

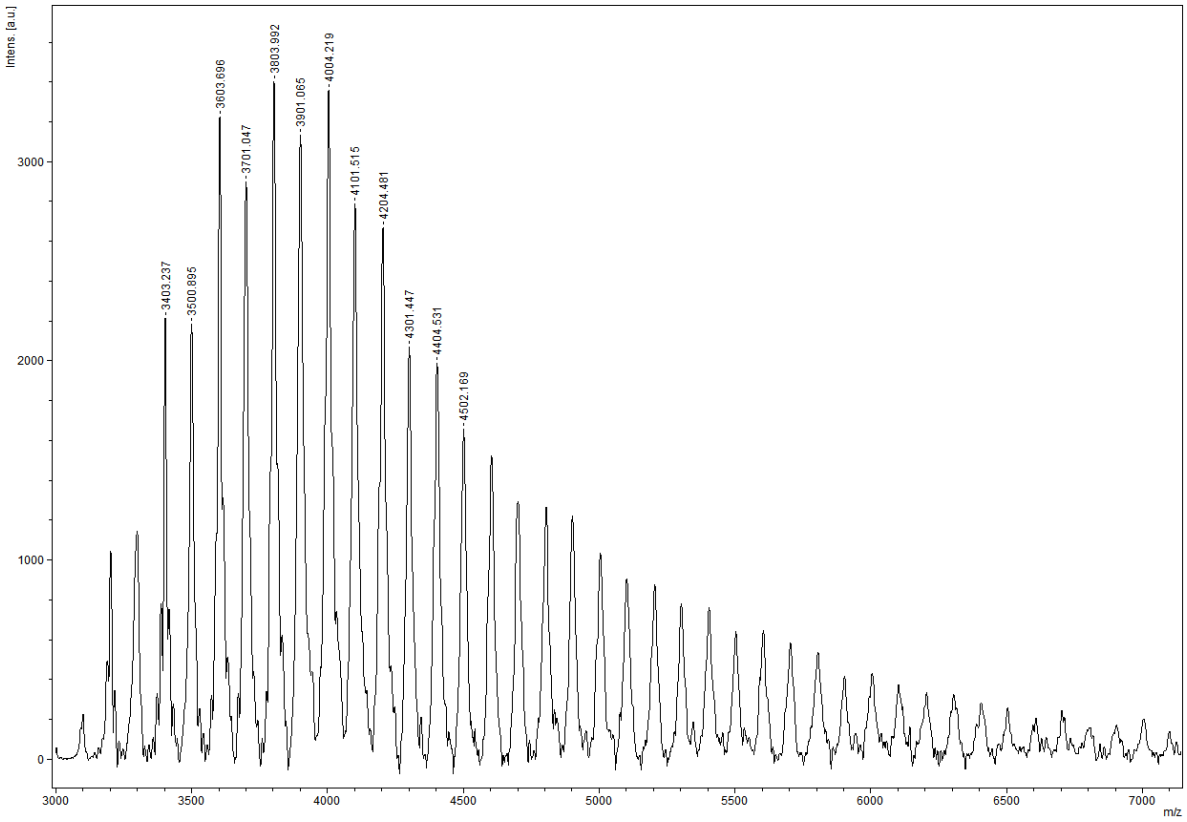


Figure 12. MALDI data for compound 12.

4. Future Work

The goal is to eventually take the synthesis route from Section 2.5 and add one more step. This additional step would be to make 2-bromo-3-[2-(2-methoxyethoxy)ethoxymethyl]-5-iodothiophene. We would do this by first brominating the 2 position on the 3-thiophenementhanol. Then we would iodinate the 5 position using N-iodosuccinimide instead of N-bromosuccinimide though with a similar procedure. This would allow us to get a better conversion of the magnesium chloride to the 5 position instead of it being at both the 2 and the 5 positions. This in turn would result in a polymer that is more regioregular. This could also be achieved however with the right Grignard reagent and reaction conditions.

We also need to do more studies involving the reaction conditions and the kinetics of these conditions for the polymerization of these monomers. This will help in terms of being able to hit target molecular weight along with narrow dispersity which we have yet to do.

Another interesting component to look at would be to alter the length of the ethylene glycol chain. Based on the mechanism in which lithium ions move through poly(ethylene glycol), one would believe that this would increase the ionic conductivity of the polymer. There are also interesting aspects as to how the phase behaviors of the polymer would change with increasing or decreasing the side chain length. This can also be said for changing the length of the alkyl chain of the 3-octylthiophene. It would be interesting to see how the length of the alkyl chain affects the phase behavior of the random copolymer versus how it affects the block copolymer. This is because changing the length of the alkyl chain will affect the solubility of the polymer.[4]

In addition, another fundamental question that can be answered with this work is what types of applications will these polymers be best suited for. Does the random copolymer perform better in sensor application whereas the block copolymer is better for batteries and supercapacitors?

5. Conclusion

The synthetic routes for two different monomers have been successfully identified. We have obtained clean product of 2,5-dibromo-3-[2-(2-methoxyethoxy)ethoxy]thiophene and 2,5-dibromo-3-[2-(2-methoxyethoxy)ethoxymethyl]thiophene. We have also identified what condition lead to stability issues with these monomers. Ideally, we would like to have an iodine

in the 5 position and a bromine in the 2 position for these monomers. More work stills needs to be done with regards to understanding the kinetics of the polymerization, as well as the right reaction conditions in order to hit target molecular weight and regioregularity of these polymers.

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