Identifying a Synthetic Method to Achieve Higher Molecular Weight Soluble Conductive Polymers

Conductive polymers are long chains of organic molecules that contain an unusual 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.

Conventional energy sources are rapidly depleting day by day, leading to the need of 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 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.

Our overall goal is to understand how changes in chemical structure affect polymerization and what molecular weights are achievable. The conductive polymers that we are using are derived from thiophene. Addition of ether substituents increases electron density, reducing oxidation potential and increasing polymer electrochemical stability.[6] Long alkyl chains are added to impart solubility, which will aid in polymer processing. We will test different polymerization techniques on different monomers to determine which produces the highest molecular weight polymers.

Methods: For my research project I will be synthesizing soluble, electron-rich conductive polymers derived from thiophene. This will require synthesis of three different monomers and polymerization of them using various polymerization techniques. The monomers that I will be preparing are 3,4-(2-dodecylethylenedioxy)thiophene (EDOT-C_{12}, a more soluble derivative of thiophene; Figure 1), 2,5-dibromo-[3,4-(2-dodecylethylenedioxy)]thiophene-C_{12} (Br_2EDOT-C_{12}, Figure 2), and 3,4-dihexyloxythiophene (3,4-DHOT, a more symmetrical thiophene to help prevent specific defects; Figure 3) all shown in the reaction schemes below. Once the monomers are made, I will be polymerizing them in addition to 3-hexylthiophene which will be used as a baseline comparison, using direct arylation polymerization (Figure 4) and Grignard metathesis polymerization (Figure 5). My research will be aided by a graduate student who has already prepared PEDOT-C_{12} via chemical oxidative polymerization (Figure 6).

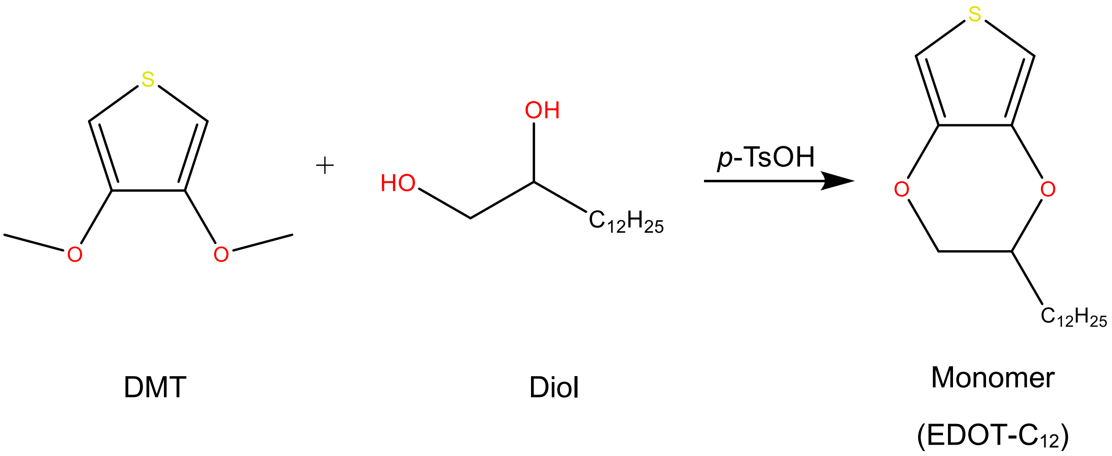

Figure 1. Monomer synthesis of EDOT-C12 via transetherification between 3,4- dimethoxythiophene (DMT) and 1,2-tetradecanediol.

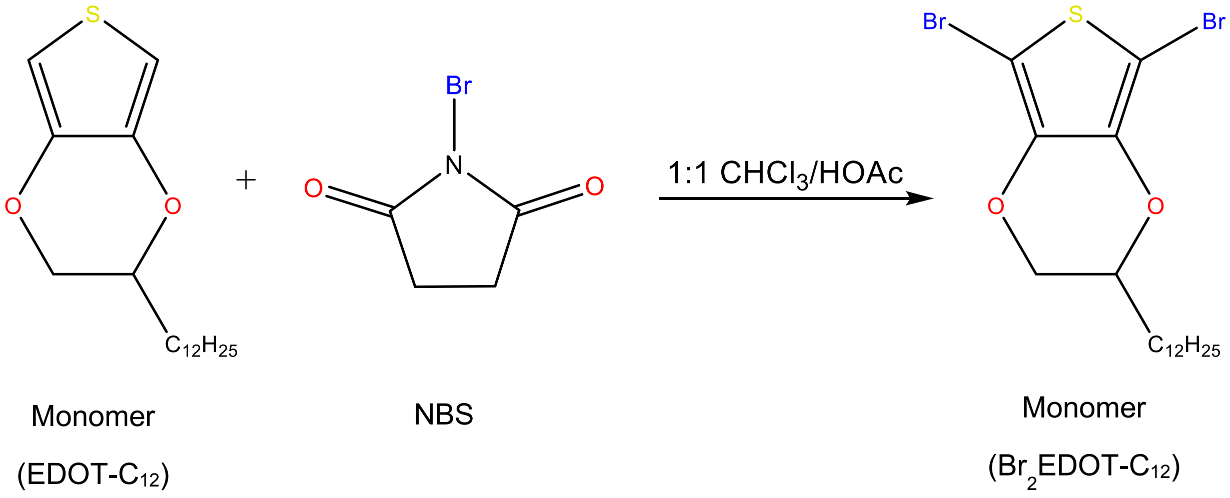

Figure 2. Monomer synthesis of $Br_2EDOT-C_{12}$ via bromination of $EDOT-C_{12}$ using n-bromosuccinimide (NBS).

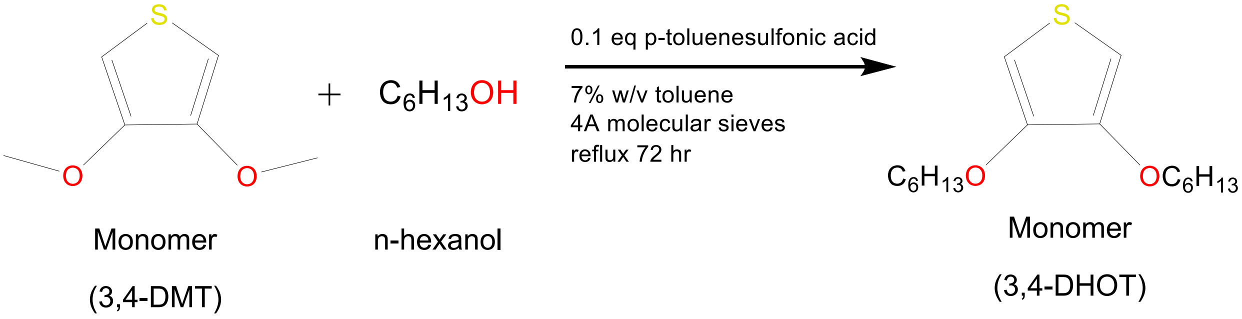

Figure 3. Monomer synthesis of 3,4-DHOT via transetherification between 3,4- dimethoxythiophene (3,4-DMT) and n-hexanol.

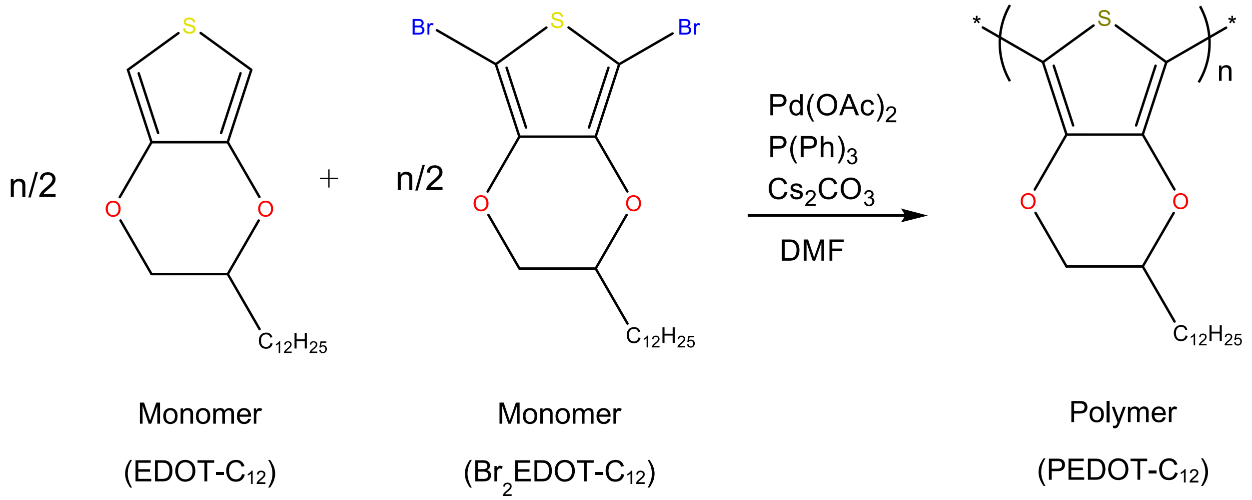

Figure 4. Synthesis of poly(EDOT-C_{12}) via direct arylation reaction between EDOT-C_{12} and Br_2EDOT-C_{12}.

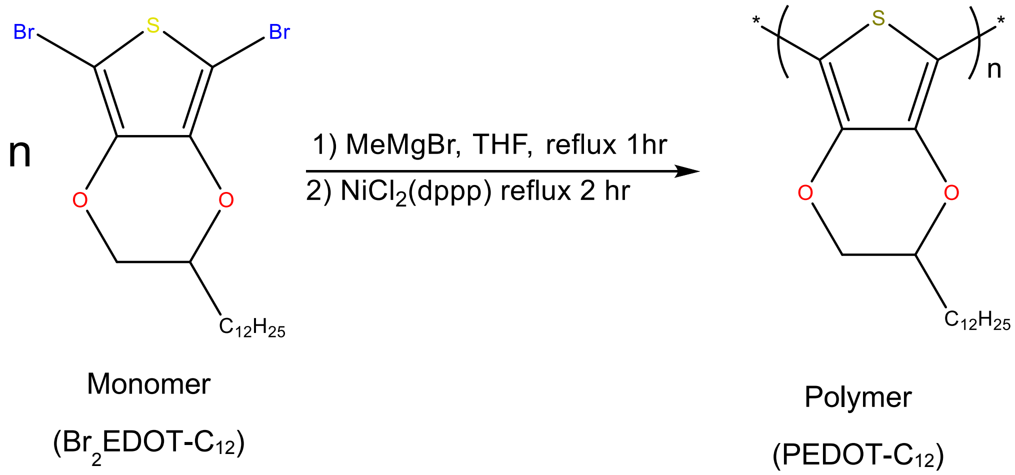

Figure 5. Polymer synthesis of poly(EDOT-C_{12}) via Grignard metathesis of Br_2EDOT-C_{12}.

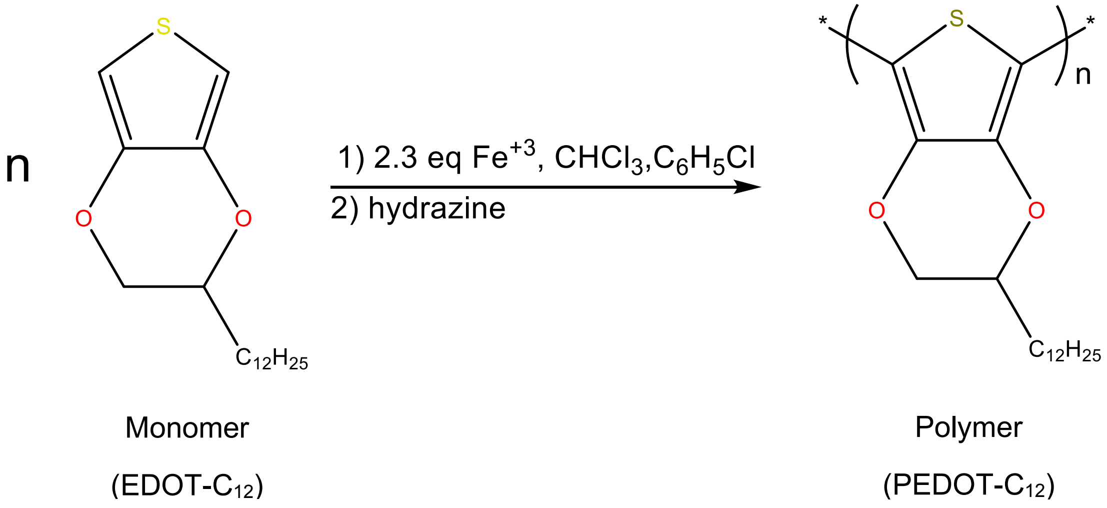

Figure 6. Polymer synthesis of poly(EDOT-C_{12}) via chemical oxidation of EDOT-C_{12}.

Analysis: All monomers will be analyzed using nuclear magnetic resonance (NMR) spectroscopy, which is used to identify the purity and structure of the monomer. Depending on the NMR results, I will either proceed to polymerization or further purify the monomer using techniques such as recrystallization, column chromatography, or reprecipitation. Once the initial monomer (EDOT-C_{12}) is prepared and purified, the second monomer (Br_2EDOT-C_{12}) will be analyzed using NMR and mass spectrometry, which will help to determine the exact molecular weight and structure of the monomer. After both monomers have been purified, they will be polymerized as shown in Figures 4 and 5. The resultant polymers will be analyzed using gel permeation chromatography (GPC), which will determine the polymers' molecular weights.

Interpretation and possible findings: A comparison of the molecular weights of the polymers prepared using the two methods will be made. Depending on the results from the GPC testing we will find out the molecular weight of our polymer which will determine whether our polymerization produced a high molecular weight polymer or not. Our chemical oxidative polymerization of EDOT-C_{12} has already produced PEDOT-C_{12} with molecular weight of 12,560 g/mol, equating to 41 repeat units (determined by dividing the polymer weight by the molecular weight of the repeat unit). We anticipate that the direct arylation polymerization and Grignard Metathesis polymerization will yield higher molecular weights.

Cited Literature

1. *Benefits of Renewable Energy Use*; Union of Concerned Scientists: UCS, 2017.
2. *Crystalline Silicon Solar Cell*; Science Direct, 2012.
3. Wong, W-Y.; Ho, C-L. "Organometallic Photovoltaics: A New and Versatile Approach for Harvesting Solar Energy Using Conjugated Polymetallaynes," *Acc. Chem. Res.* **2010,** 43 (9), 1246-1256.
4. Tapan K. & Smita P., "Review on Conducting Polymers and Their Applications," *Polymer-Plastics Technology and Engineering* **2012,** 51 (14), 1487-1500.
5. Ayalew, H. *et al., Synlett* **2018,** 29, 2660-2668.

Timeline:

FALL 2019: Complete synthesis and purification of each monomer to be used for polymerization. Characterize each monomer using nuclear magnetic resonance spectroscopy and mass spectrometry.

SPRING 2020: Each monomer (3HT, EDOT-C_{12}, Br_2EDOT-C_{12}, 3,4-DHOT, $Br_2$3,4-DHOT) will be polymerized using direct arylation polymerization and Grignard metathesis polymerization. Gel permeation chromatography will be used to determine polymer molecular weights. Interpretation of gel permeation chromatography data will be accomplished by comparison to polystyrene standards.

SUMMER 2020:

Optimize reaction conditions for polymerization techniques to achieve higher molecular weight conductive polymers made from the above monomers. The polymers will undergo gel permeation chromatography as well to determine if current methods used have been achieving higher molecular

weights before proceeding with more polymerizations. Br_2-containing monomers will undergo optimization of reaction conditions to maximize product purity.

If crystalline solid monomers are obtained, monomer crystal structures will be determined using single crystal X-ray diffraction. Results will be presented at the Women in Science and Engineering (WiSE) Conference and/or the Annual Undergraduate Research Conference.

FALL 2020: Polymer molecular weights from direct arylation and Grignard metathesis will be compared to polymers prepared using chemical oxidative polymerization performed in different solvents. Polymerizations will undergo further optimization if needed, or alternative polymerization methods will be tested and characterized using gel permeation chromatography.

Project Timeline:

Research will be presented at national ACS conference in Spring 2020 and WiSE conference held at Texas State. I will be continuing my research on higher molecular weight conductive polymers after my URF project as an undergraduate research volunteer. As that project matures, I will begin to use those polymers in attempts to detect genetic markers for diseases such as cancer.

Budget Narrative:

Chemicals

Items	Quantity	Amount	Total
3-Hexylthiophene, 99+% (5g)	1	$92.07	$92.07
3,4-Dimethoxythiophene, 98+% (5g)	1	$136.33	$136.33
Chloroform, 99.9+% (4L)	1	$70.37	$70.37
Chlorobenzene, 99% (2.5L)	1	$35.57	$35.57
1,3-Bis(diphenyl-phosphine)propane-nickel(II) chloride, 99+% (5g)	1	$71.25	$71.25
Chloroform-D, 99.6+% (100mL)	1	$70.66	$70.66
Methyl-magnesium bromide, 35% ~3M in ethyl ether (250g)	1	$125.35	$125.35
N-Bromo-succinimide (250g)	1	$63.25	$63.25
Palladium acetate, 99.9+% (1g)	1	$74.84	$74.84
Tetrahydrofuran, anhydrous, 99.5+% (1L)	1	$116.28	$116.28
N,N-dimethylformamide, 99.8+% (4L)	1	$46.50	$46.50
Total			$902.47

Materials

Item	Quantity	Amount	Total
Syringe filters, PTFE, 25mm, 0.45um (100 pack)	1	$89.32	$89.32
Medium nitrile gloves (50 pack)	1	$7.50	$7.50
Total			$96.82

Item	Amount
Chemicals	$902.47
Materials	$96.82
Total	$999.29

The requested funds will be utilized for the purchase of chemicals, materials and fees associated with the synthesis of higher molecular weight conductive polymers.

The chemicals required for the reactions in the synthesis of higher molecular weight conductive polymers are 3-hexylthiophene (3HT) and 3,4-dimethoxythiophene (3,4-DMT). 3HT is needed to be used as a baseline comparison to other monomers when used in various polymerizations. 3,4-DMT is required for the monomer synthesis 3,4-dihexyloxythiophene (3,4-DHOT) to be used in various polymerizations. $CHCl_3$, C_6H_5Cl, and NBS are required to carry out the monomer synthesis of the materials previously mentioned. DMF, THF, $Pd(OAc)_2$, MeMgBr, and $NiCl_2$(dppp) are also required to carry out the various polymerization techniques of the materials mentioned before.

The materials required for this project consist of nitrile gloves which are always required during lab. Syringe filters are required for filtering polymer samples dissolved in chloroform and later used for characterization through gel permeation chromatography.