

THREE-DIMENSIONAL PRINTING OF POLYISOPRENE-BLOCK-POLYSTYRENE-
BLOCK-POLY(3-HEXYLTHIOPHENE)

by

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To my twin sister, Ashley D. Niermann.

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by

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THESIS

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My family—thank you for letting me do whatever I wanted. I have learned some hard lessons the hard way, but I would never have become successful without you. Thank you, Ashley, for being the only person who understands me; we did it.

May 2017

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The University of Texas at Dallas, 2017

Supervising Professor: Dr. Mihaela C. Stefan

The goal of my thesis is to explore the limitations of three-dimensional printing on elastomeric block copolymers containing poly(3-hexylthiophene) by studying the extrusion of polyisoprene-*b*-polystyrene-*b*-poly(3-hexylthiophene). The triblock copolymer was synthesized through an anionic coupling mechanism from an allyl-terminated poly(3-hexylthiophene) and polyisoprene-*b*-polystyrenyl anion. The triblock copolymer was characterized with ^1H NMR, size exclusion chromatography (SEC), and bottom-gate bottom-contact organic field effect transistors (OFET). The material was successfully synthesized and purified and contained 9 mole% poly(3-hexylthiophene), 68 mole% polyisoprene, and 23 mole% polystyrene. Although the material exhibited relatively low mobility, it was readily extruded with a custom pneumatic extruder at room temperature. The results legitimize the potential use of this material for three-dimensional printing applied in flexible electronics.

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CHAPTER 1

INTRODUCTION

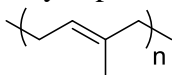
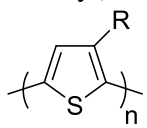
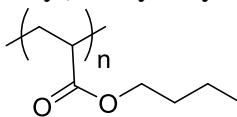
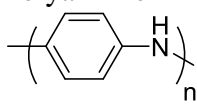
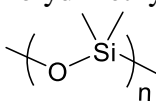
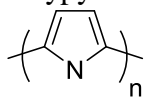
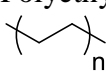
Three-dimensional printing is an engineering tool that allows for a more efficient prototyping and design process.¹⁻³ Furthermore, three-dimensional printing has proven to be a useful technology for creating molds, tools, and even electronic devices.²⁻⁵ However, the types of materials useful for three-dimensional printing are limited by the extrusion (i.e printing) method.⁴ The most commonly used printing method is where a material is pushed through a nozzle with filament-driver motors or pressure.⁶ To extrude a material in this way the material must meet a rheological requirement in that it must exhibit an appropriate viscosity.⁷ A simple solution to this problem is to heat the material to its melting temperature to achieve an appropriate viscoelastic behavior, such that the material can be extruded while maintaining some level of structural integrity. However, the application of heat excludes materials with high melting points and materials that are sensitive to high temperatures. Furthermore, once the material is extruded the polymer should adhere to a surface and itself. Overcoming all these engineering requirements, the usefulness of three-dimensional printing, ultimately, is defined by the final product. Therefore, the usefulness of a material is not only determined by its printability but also its function after it has been printed.

As of now, technology is trending towards advancing flexible electronics that could be useful in responsive robot skin, wearable devices, solar cells, and flexible charge storage devices.⁸⁻
¹⁰ However, flexibility and conductivity are generally incompatible properties, such that a material that is conductive is not very flexible and vice versa.⁸ In most instances, research has focused on

finding an optimal balance between conductivity and flexibility through the fabrication of the material.

In general, flexible electronics are fabricated via composite materials.¹¹⁻¹⁶ More specifically, a conducting substance, which can be metallic or organic, is dispersed throughout an elastomeric matrix, such as polydimethylsiloxane, polyurethane, or polyisoprene (see Table 1.1).^{14,17} ¹⁸Another way to obtain a material that is both elastic and conducting is through the synthesis of block copolymers which allows for the improvement or introduction of new properties to a homopolymer.¹⁹ Furthermore, the synthesis of block copolymers offers the ability to tune the overall properties of a material.²⁰

Table 1.1. Properties of Materials Used in Flexible Electronics

Conducting Material	Conductivity (Scm ⁻¹) ^{21,22}	Elastic material	T _g (°C) ²³	E _b /%*
Inorganic				
Ag	6 x 10 ⁵	Polyisoprene 	-72	750-850
Organic				
Semiconducting Polymers[‡]				
rr-Poly(3-alkylthiophene) 	1 - 10 ³	Poly(<i>n</i> -butylacrylate) 	-54	2000
Polyaniline 	30 - 200	Polydimethylsiloxane 	-125	400-800
Polypyrrole 	10 ² - 2 x 10 ³	Polyethylene 	-125	100-1000

*E_b: Represents an elastic property called percent of mechanical elongation for each polymer⁹

[‡]Conductivity of semiconducting polymers are shown when they are in the doped state.

The overall electronic and mechanical properties of polymers are defined by the molecular weight, polydispersity index, and the polymer microstructure; all of which can be controlled synthetically through reactive intermediates (i.e. anions, cations, and radicals).²⁰ Additionally, the microstructure can be adjusted by changing reaction conditions such as solvent polarity, temperature, and mode of propagation.²⁴ The synthetic control over the molecular weight and microstructure allows us to tune the morphology of the phase separation behavior of the block copolymers.^{19,25,26} Specifically, block copolymers that exhibit both conductivity and elasticity are, usually, rod-coil block copolymers, in that the conducting polymer block forms a rigid-rod polymer chain while the elastic block forms more of a flexible-coil polymer chain (Figure 1.1). The result of covalently bonding these two different chain structures (as opposed to forming a blend between the homopolymers) is a series of distinct phase separated morphologies (Figure 1.2).²⁶ The morphology of a block copolymer can be varied by adjusting the mole percent composition of each block.^{27,28}

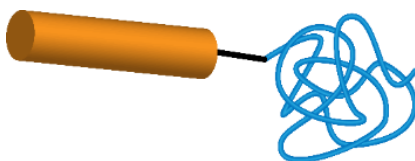


Figure 1.1. Illustration of a rod coil-block copolymer

The morphology of the block copolymer can be used to enhance the electronic or mechanical properties so that the conductivity can be maintained even with the incorporation of an insulating segment (Table 1.2).²⁹⁻³¹ For example, a triblock copolymer of poly(3-hexylthiophene)-*block*-polystyrene-*block*-polyisoprene with a mole composition of 24:44:32, respectively, can maintain a conductivity of $2 \times 10^{-2} \text{ Scm}^{-1}$.³⁰ Furthermore, semiconducting elastomeric block copolymers are able to maintain a conductivity after being stretched in one

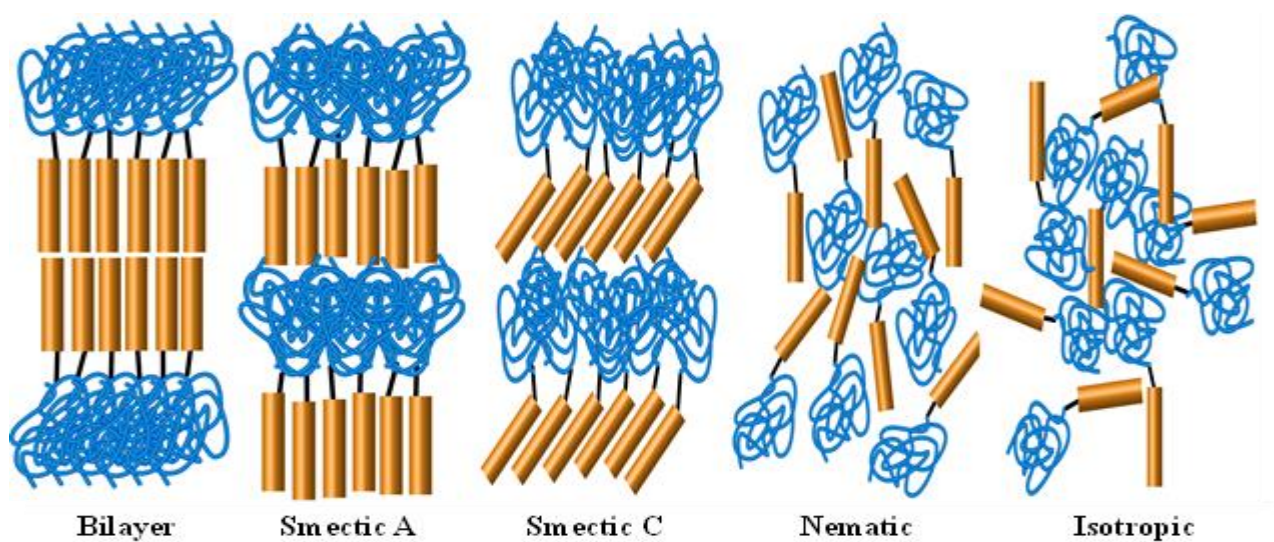


Figure 1.2. Phase separation behavior for rod-coil block copolymers.

direction (i.e. strained). For instance, polypyrrole polymerized on the surface of polyurethane can maintain a conductivity $1.20 \times 10^{-1} \text{Scm}^{-1}$ after experiencing strains up to 50%.³² These observations are similar with those of polyaniline when grafted to poly (styrene-*co*-ethylenebutylene-*co*-styrene), in that the material is able to maintain a conductivity up to $1.5 \times 10^4 \text{Scm}^{-1}$ while experiencing strain up to 20%.³³ Notably, the polyaniline-*b*-poly(styrene-*co*-ethylenebutylene-*co*-styrene) was able to maintain conductivity with strains over 100 % when the composition of polyaniline was reduced.³³ Therefore, the approach to using block copolymers is a promising strategy in order to obtain a material for flexible electronics.

Table 1.2. Properties of Semiconducting Elastomeric Block Copolymer

Block copolymer	Conductivity (Scm^{-1})	Max Strain
Polypyrrole- <i>b</i> -Polyurethane	1.2×10^{-1}	50%
Polyaniline- <i>b</i> -Poly(styrene- <i>co</i> -ethylenebutylene- <i>co</i> -styrene)	1.5×10^4	20%
Poly(3-hexylthiophene)- <i>b</i> -Polystyrene- <i>b</i> -Polyisoprene	2×10^{-2}	-

Of the block copolymers that are suitable for flexible electronics, polythiophene based materials are relatively unexplored. Specifically, poly(3-alkylthiophene)s are a class of commercially available semiconducting polymers known for their processability and great solubility in organic solvents.³⁴ Poly(3-alkylthiophene)s are known for their high charge carrier mobility.³⁴ The high charge carrier mobility is mainly a consequence of the regioregularity (i.e. the monomer units add head to tail during polymerization. Refer to Figure 1.3). The regioregularity produces a nanofibril morphology, which enables charge carrier hopping mechanisms through the π - π stacking (the co-facially stacked polymer backbones) (Figure 1.4).^{35,36}

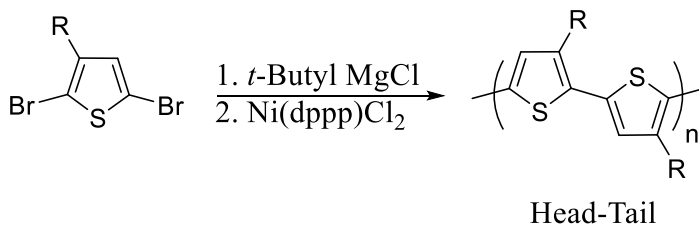


Figure 1.3. Synthesis of regioregular poly(3-alkylthiophenes) through GRIM.

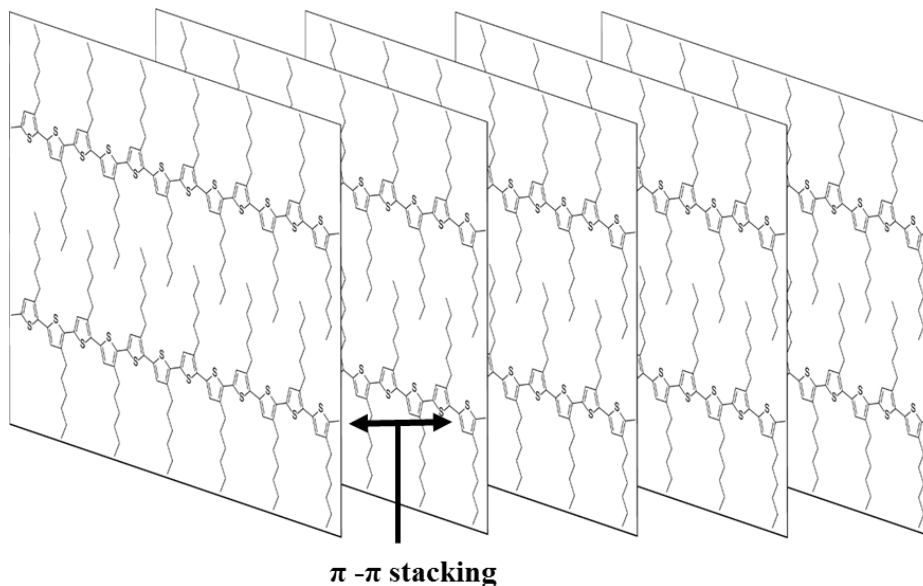


Figure 1.4. The π - π stacking between the polymer backbones.³⁶

Poly(3-alkylthiophenes) are popularly synthesized through Grignard Metathesis (GRIM) which does not require cryogenic temperatures and produces a high composition of regioregular poly(3-alkylthiophene)s (Figure 1.3).^{37,38} Most importantly, the polymerization through GRIM is quasi-“living,” in that poly(3-alkylthiophene)s produced through GRIM have well defined molecular weights and can undergo end-group functionalization.^{37,39} Thus, poly(3-alkylthiophenes) can be readily used to make well defined block copolymers.

Block copolymers containing a semiconducting segment, like poly(3-alkylthiophene), are commonly characterized with organic thin film field effect transistors.⁴⁰ Field effect transistors are electronic devices that characterize the performance of a semiconductor based on the material's charge carrier mobility (μ), threshold voltage (V_T), and the current on-off ratio. Field effect transistors are fabricated with two configurations: bottom-gate bottom-contact or bottom-gate top-contact (see Figure 1.5).^{41,42} With either configuration, the material is tested by applying a sweeping voltage to the gate electrode with a constant bias voltage on the drain electrode. The current is monitored at the drain electrode during the voltage sweep, generating a transfer curve. From the transfer curve, we can extract information to calculate the carrier mobility using Equation 1.1, where I is the current monitored at the drain electrode, C is the capacitance of the dielectric layer, and V is the voltage at the gate and threshold. The mobility is a representation of how well a semiconductor carries charges such that a large mobility will lead to better device performance. Furthermore, the threshold voltage and on-off ratios are helpful in describing the sensitivity of the device.

$$\mu = \frac{2 \times \text{Length}_{\text{channel}} \times I_{\text{Drain}}}{\text{Width}_{\text{channel}} \times C \times (V_{\text{Gate}} - V_{\text{Threshold}})^2} \quad \text{Equation 1.1}$$

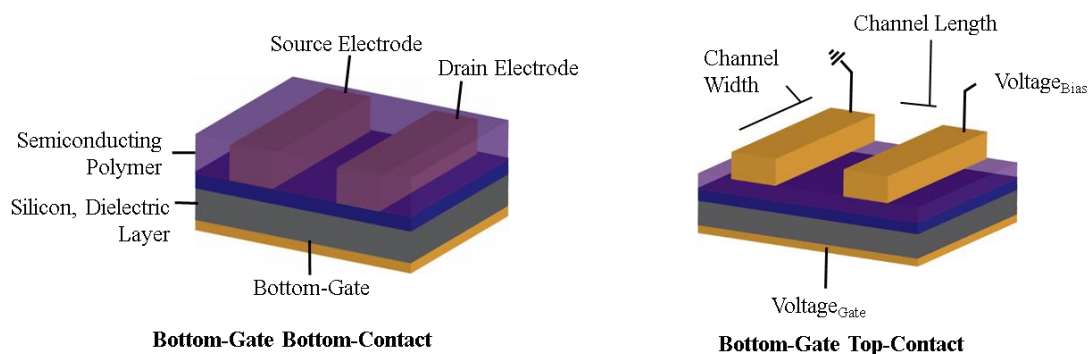


Figure 1.5. Schematic diagram of field effect transistors (OFET).

Block copolymers of polythiophenes and their derivatives have been extensively used in electronic applications including photovoltaics, organic field effect transistors, and batteries.⁴³⁻⁴⁵ However, there is not a lot of utilization of poly(3-alkylthiophene) based block copolymer materials in actuator technology, which require a material to be both conducting and elastic. Poly(3-alkylthiophene) based elastomeric block copolymers maintain conductivity with the presence of an insulating block, yet, the mechanical properties have not been well defined.^{30,46} Thus, the use of poly(3-alkylthiophene)s demonstrates legitimate potential and their applications in flexible electronic technology have yet to be realized.

CHAPTER 2

EXPERIMENTAL SECTION

2.1 Materials

All materials were purchased from Sigma-Aldrich or Fischer Scientific. Solvents were collected via reflux over sodium/benzophenone. All monomers were distilled over CaH prior to use, and other chemicals were used as received. Each polymerization reaction was performed under nitrogen atmosphere and all glassware were dried at 120°C for at least 24h prior to use.

2.2 Characterization

Synthesized substances were analyzed with proton nuclear magnetic resonance (^1H) spectra which were recorded in CDCl_3 on Bruker AVANCE III 500 spectrometer (500 MHz) at 25 °C.

Size exclusion chromatography (SEC) was carried out on a Viscotek VE 3580 system equipped with ViscoGEL columns (GMHHR-M), connected to a refractive index (RI) detectors. SEC solvent/sample module (GPCmax) was used with HPLC grade THF as the eluent, and calibration was based on polystyrene standards.

Matrix Assisted Laser Desorption Ionization Time of Flight (MALDI-TOF) was performed on a Shimadzu Biotech Instrument fitted with a 266 nm laser. Data acquisition was in linear mode. The MALDI plate was calibrated with monoisotopic proteins, myoglobin and cytochrome c, with concentrations of 1 mg/mL in 50:50 HPLC grade water and 1% formic acid in acetonitrile using α -cyano-4-hydroxycinnamic acid as the matrix. The polymer samples were prepped at a target concentration of 1 mg/mL using 2,2':5',2''-terthiophene as the matrix.

Bottom-gate bottom-contact organic thin film transistors were fabricated using a previously published standard protocol.⁴⁷ The polymer sample was prepared at a concentration of 1 mg/mL and was filtered through a 0.2µm filter. The polymer sample was drop-cast on the devices. Mobility measurements were made on a Keithley 4200-SCS semiconductor characterization system with a Cascade Microtech Model Summit Microchamber probe station. The measurements were made at room temperature under normal atmosphere.

2.3 Synthetic Methods

2.3.1 Synthesis of 2,5-dibromo-3-hexylthiophene

To a three-neck 1 L round bottom flask fitted with a condenser, 73 g of 3-bromothiophene (0.44 mole) was added to 400 mL of ether under nitrogen atmosphere at 0°C. Then, 0.25 g of dichloro (1,3-bis(diphenylphosphino)propane)nickel (Ni(dppp)Cl₂) (0.042 mole) was added to the flask. Then, 220 mL of 1-hexyl magnesium bromide (0.44 mmole) was added dropwise to the reaction vessel. After all the Grignard reagent was completely transferred, the reaction was heated under reflux at 40 °C. The reaction was quenched over acidified ice. The solution was washed with a saturated solution of sodium chloride. The organic layer was collected and dried over anhydrous magnesium sulfate. ¹H NMR (500 MHz, CDCl₃): 0.86 (t, 2H), 1.27 (m, 6H), 1.5 (m, 2H), 2.47 (t, 2H), 6.90 (dd, 1H), 6.94 (s, 1H), 7.25 (dd, 1H) Yield: 95%

The crude product (40 g) was taken in a 1 L single neck round bottom with 250 mL of glacial acetic acid and 250 mL of chloroform at 0 °C. Then, 83.4 g of N-bromosuccinimide (0.41 moles) was added slowly to the reaction mixture. The bromination was monitored with a gas chromatograph fitted with a mass spectrometer detector. When all the monomer was converted to dibrominated product, the reaction was poured over ice. The solution was washed with a saturated

solution of sodium chloride. The organic layer was collected and dried over magnesium sulfate. The pure dibrominated product was obtained via vacuum distillation and column chromatography. ^1H NMR (500 MHz, CDCl_3): ^1H 0.86 (t, 2H), 1.27 (m, 6H), 1.5 (m, 2H), 2.47 (t, 2H), 6.74 (s, 1H). 67 g of clear oil was covered (Purity 98%, Yield 92%)

2.3.2 Synthesis of Allyl-terminated poly(3-hexylthiophene) by Grignard Metathesis (GRIM)

To a flame dried, 250 mL 3 neck round bottom flask kept under nitrogen the following chemicals were added- 10 mL of dried THF, 1.0 mL of 2,5-dibromo-3-hexylthiophene (5.0 mmole) and 2.6 mL of *t*-butyl magnesium chloride (5.0 mmole). After 2 hours, a GC-MS chromatogram confirmed 80 % monomer conversion. Then, 40 mL of dried THF was added to the flask. Following the addition of THF, 34 mg $\text{Ni}(\text{dppp})\text{Cl}_2$ catalyst (6.3×10^{-2} mmole) was poured into the flask. After 5 minutes, 2 mL allyl magnesium bromide was injected into the flask. After 20 minutes, the reaction mixture was quenched with a solution of dimethyl glyoxime and ethanol. The purple precipitate was collected in a cellulose thimble via gravity filtration. The collected precipitate was washed through Soxhlet extractions in the following order: methanol, hexane, and chloroform. ^1H NMR (500 MHz, CDCl_3): ^1H 0.9 (t, 3H), 1.35-1.43 (m, 6H), 1.69 (t, 2H), 2.80 (t, 2H), 3.49 (d, 2H), 5.11 (m, 2H), 5.98 (m, 1H) 6.95 (s, 1H). SEC: M_n = 8,000 g/mol; PDI: 1.3

To prevent any side reactions with the bromine end-group, the allyl terminated poly(3-hexylthiophene) was reacted with excess *t*-butyl magnesium chloride. A typical reaction procedure involved dissolving the polymer in THF under nitrogen atmosphere. Then, the grignard reagent was added in excess. The reaction was allowed to go for 3 hours and quenched in methanol. The purple precipitate was collected in a cellulose thimble and subjected to a series of Soxhlet

extractions in the following order: methanol and chloroform. A MALDI-TOF analysis was performed to determine the extent of the magnesium halogen exchange.

2.3.3 Anionic Synthesis of Polyisoprene-block-Polystyrene-block-Poly(3-hexylthiophene)

Under nitrogen atmosphere 6.0 mL of isoprene (0.06 moles) was initiated with 0.24 mL of *n*-butyl lithium in 25 mL of toluene. The anionic reaction was allowed to run for 2 hours at room temperature. A sample was taken after 3 hours, which was followed by the addition of 0.5 mL of styrene (4.4 mmole). The solution turned a transparent orange with addition of styrene. After 20 minutes, a sample was taken, and then 30 mL allyl terminated poly(3-hexylthiophene) in THF (0.68 g of polymer in 30 mL THF) was transferred to the reaction flask. The reaction was allowed to go for 1 hour before it was quenched in methanol. The purple precipitate was collected in a cellulose thimble via gravity filtration and subjected to a series of Soxhlet extractions in the following order: methanol, hexane, and chloroform. The block copolymer was extracted with hexane, as was evident by the purple color of the dried polymer material. To remove any residual homopolymer, the hexane extracted material was washed with cold cyclohexane. Polyisoprene-*b*-polystyrene: ^1H NMR (500 MHz, CDCl_3): ^1H 1.4 (t, $J = 7$ Hz, 3H), 1.53 (s, 3H), 1.61 (s, 3H), 1.67 (s, 3H), 2.0 (m, 2H) 4.7 (m, 1H), 5.1 (m, 1H), 6.5 (m, 2H) 7.1 (m, 3H), SEC: $M_n = 11,000 \text{ g/mol}$; PDI = 1.2.

2.4 Three-Dimensional Printing of Polyisoprene-*b*-Polystyrene-*b*-Poly(3-hexylthiophene)

The three-dimensional printing of the polymer sample was performed at room temperature through a 27-gauge (0.21 mm diameter) syringe tip. The synthesized material was extruded through a custom pneumatic extruder designed by our collaborators. The synthesized polymer sample was printed as is and was not modified with any additives.

CHAPTER 3

RESULTS

3.1 Synthesis of the monomer 2,5-dibromo-3-hexylthiophene

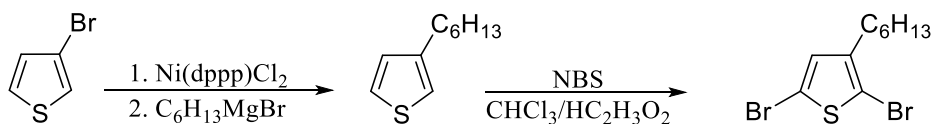


Figure 3.1. Synthesis of 2,5-dibromo-3-hexylthiophene.

The monomer 2,5-dibromo-3-hexylthiophene was synthesized from 3-hexylthiophene with N-bromosuccinimide, as illustrated in Figure 3.1. The proton NMR of the purified 2,5-dibromo-3-hexylthiophene product is shown in Figure 3.2. From the NMR, there is a singlet at 6.74 ppm that integrates to 1 hydrogen that corresponds to the aromatic hydrogen. The hydrogens that correspond to the alkyl chain are identified as the triplet at 2.47 ppm that integrates to 2 hydrogens, a multiplet at 1.5 that integrates to 2 hydrogens, a multiplet at 1.27 that integrates to 6 hydrogens, and a triplet at 0.86 ppm that integrates to 3 hydrogens. The relative purity of the product is approximately 98%.

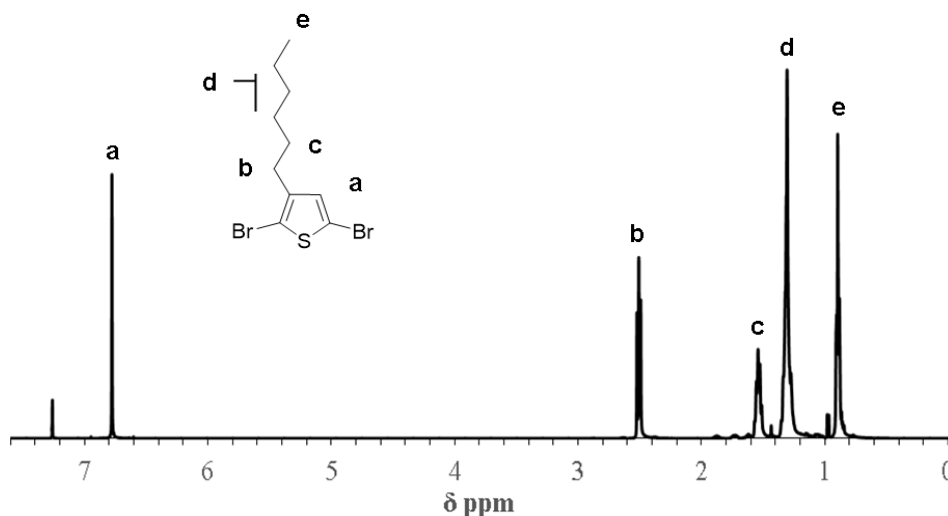


Figure 3.2. Proton NMR of the purified monomer 2,5-dibromo-3-hexylthiophene.

3.2 Synthesis of Allyl-terminated poly (3-hexylthiophene)

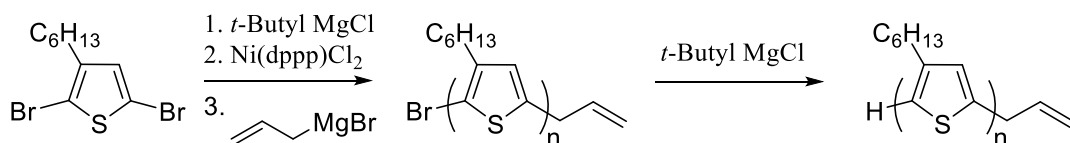


Figure 3.3. Synthesis of allyl-terminated poly(3-hexylthiophene).

The purified 2,5-dibromo-3-hexylthiophene was used to produce end group functionalized allyl-terminated poly(3-hexylthiophene) through Grignard metathesis, as illustrated in Figure 3.3. The proton NMR spectrum of the extracted product is illustrated in Figure 3.4. The proton NMR shows the presence of the allyl end group with the doublet at 3.5 ppm that integrates to 2 hydrogens, the doublet of doublets at 5.15 ppm that integrates to 2 hydrogens, and the multiplet at 5.95 ppm that integrates to 1 hydrogen.

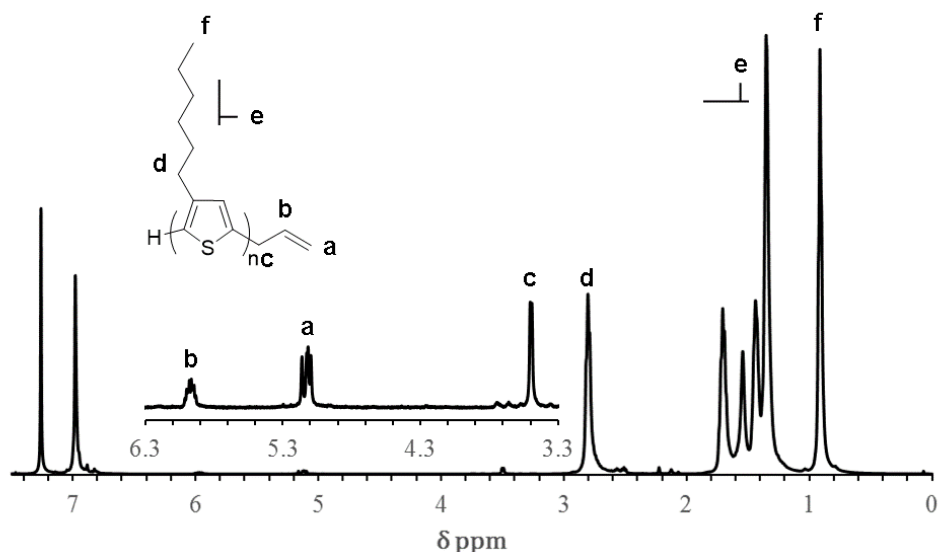


Figure 3.4. Proton NMR of allyl-terminated poly(3-hexylthiophene).

The relative distribution of the end-groups on the polymer chains are detected with MALDI-TOF, shown in Figure 3.5. With closer inspection, there are four series of peaks corresponding to the following type of end groups: H/H at $m/z = 5319$ $[(166.16 \times 32) + 2]$, H/Allyl at $m/z = 5359$ $[(166.16 \times 32) + 42]$, H/Br at $m/z = 5398$ $[(166.16 \times 32) + 80.9]$, and Br/Allyl at $m/z = 5438$ $[(166.16 \times 32) + 120.9]$. The MALDI-TOF spectra in Figure 3.5 and Figure 3.6 illustrate the disappearance of peaks at a mass to charge ratio of 5438 and 5398, which correspond to polymer chains with brominated end groups. Based on the relative intensity of the peaks, 75% of the polymer material contains an allylic end-group. Furthermore, the MALDI-TOF spectrum elucidates the number average molecular weight is approximately 6,000 KDa.

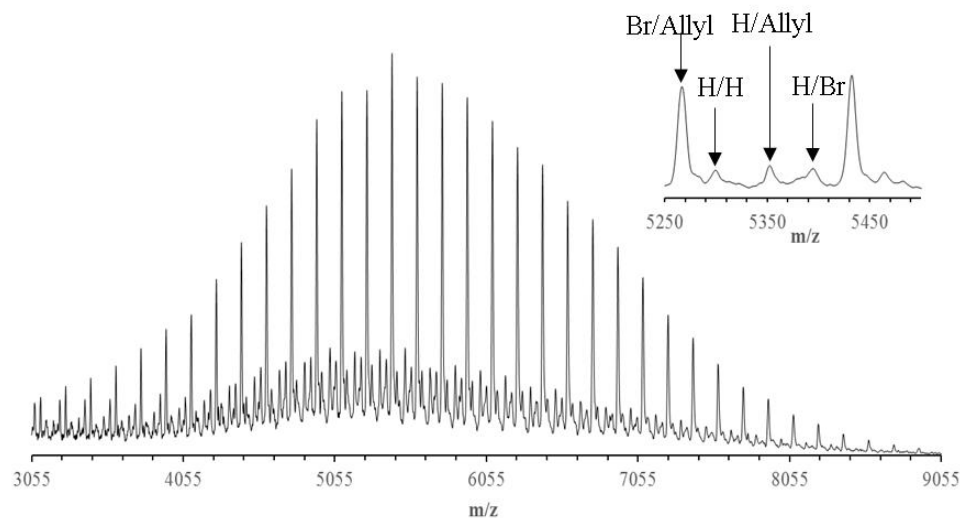


Figure 3.5. MALDI-TOF spectrum of ally-terminated poly(3-hexylthiophene).

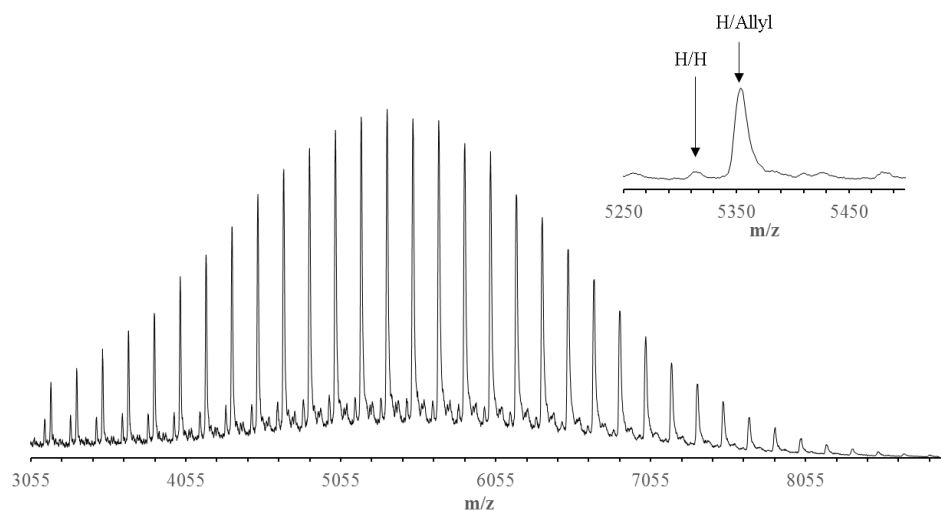


Figure 3.6. MALDI-TOF spectrum of allyl-terminated poly(3-hexylthiophene) after the magnesium halogen exchange.

3.3 Polyisoprene-*block*-Polystyrene-*block*-Poly(3-hexylthiophene)

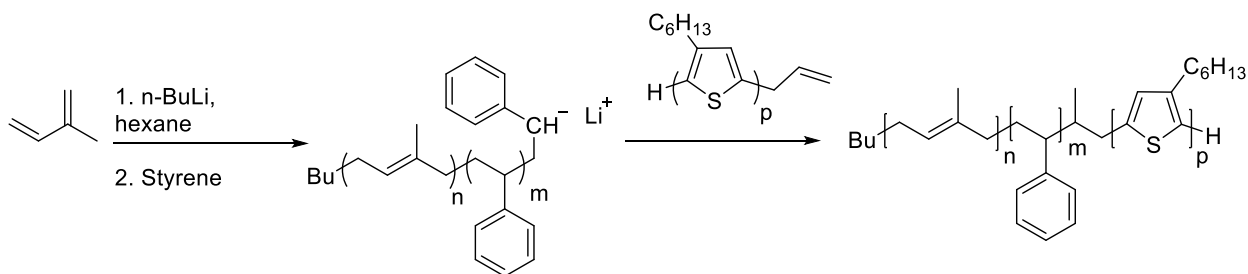


Figure 3.7. Anionic coupling reaction to produce polyisoprene-*block*-polystyrene-*block*-poly(3-hexylthiophene)

The allyl-terminated poly(3-hexylthiophene) was coupled to polyisoprene-*b*-polystyrenyl anion through an anion coupling mechanism, shown in Figure 3.7. The purified triblock copolymer analyzed by proton NMR is shown in Figure 3.8. From the NMR, we can see the presence of the methylene protons at 2.8 ppm, contributed from the hexyl side chain of the poly(3-hexylthiophene), the vinyl protons at 5.1 ppm, contributed from the alkenyl protons of the polyisoprene, and the aromatic protons at 6.6 ppm, contributed from the aromatic protons of the

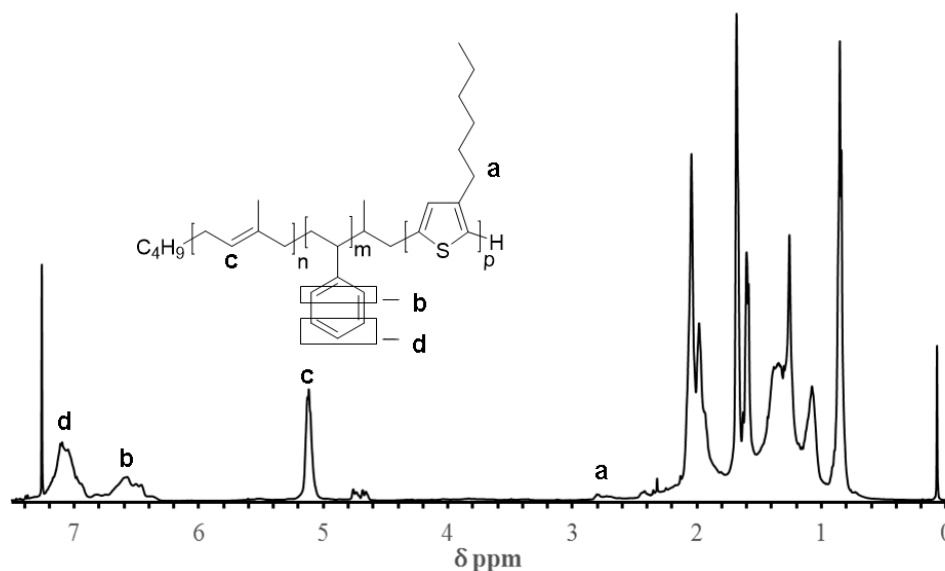


Figure 3.8. Proton NMR of the purified polyisoprene-*b*-polystyrene-*b*-poly(3-hexylthiophene).

polystyrene. With integration analysis, the mole percent composition of polyisoprene:polystyrene:poly(3-hexylthiophene) is 68:23:9, respectively. The size exclusion chromatography (SEC) of the samples taken during the reaction, as well as the purified triblock copolymer is summarized in Table 3.1. The molecular weight of the block copolymers is larger than that of poly(3-hexylthiophene) homopolymer. The molecular weights tend to decrease with the growing chain. However, the molecular weight relative to polystyrene standards with chloroform as the solvent was found to be approximately 12 KDa.

Table 3.1. Summary of Size Exclusion Chromatography

Sample	M_n	PDI
Allyl-terminated poly(3-hexylthiophene)	8,290	1.3
Polyisoprene	12,630	1.2
Polyisoprene- <i>b</i> -polystyrene	11,700	1.2
Polyisoprene- <i>b</i> -polystyrene- <i>b</i> -poly(3-hexylthiophene)	10,080	1.2
Polyisoprene- <i>b</i> -polystyrene- <i>b</i> -poly(3-hexylthiophene)*	12,043	1.2

*Molecular weight determined using chloroform with polystyrene standards

The electronic properties of the material were elucidated with bottom-gate bottom-contact organic field effect transistors; the results are summarized in Table 3.2 with literature values of poly(3-hexylthiophene) homopolymer. The average mobility of 14 devices was calculated to be $5.5 \times 10^{-6} \text{ cm}^2\text{V}^{-1}\text{s}^{-1} \pm 2.1 \times 10^{-6} \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$. The average turn-on voltage was calculated to be $220 \text{ V} \pm 92\text{V}$ and the average current on-off ratio was found to be 2.6 ± 0.98 .

Table 3.2. Summary of the Mobility Data

Sample	Mobility ($\text{cm}^2\text{V}^{-1}\text{s}^{-1}$)
Polyisoprene- <i>b</i> -polystyrene- <i>b</i> -poly (3-hexylthiophene)	$5.5 \times 10^{-6} \pm 2.1 \times 10^{-6}$
Poly (3-hexylthiophene)* ⁴⁸	10^{-2}

*Molecular weight approximated 10KDa

The material was then used for three-dimensional printing. As shown in Figure 3.9, the material was extruded to produce well resolved sinusoidal designs and linear arrays on the millimeter scale. Not only could the material be printed into complex two-dimensional structures, but also the material was printed as a simple three-dimensional architecture on the millimeter scale. The extruded material did not show any signs of creep, nor did it collapse on itself throughout the printing process.

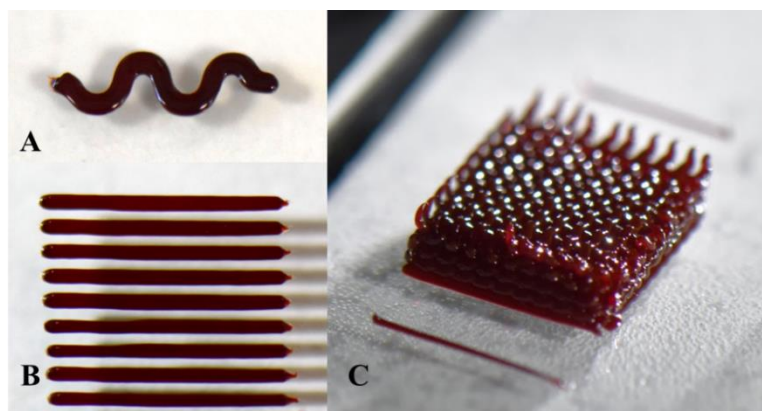


Figure 3.9. Photos of extruded triblock copolymer. A) Sinusoidal curve with dimensions of 5 x 1 mm. B) Linear array with dimensions 5 x 5 mm C) Three-dimensional grid with dimensions 5 x 5 x 5 mm.

CHAPTER 4

DISCUSSION

The purification and synthesis of the monomer 2,5-dibromo-3-hexylthiophene was successful. According to NMR analysis, the spectrum matched that of the monomer with minor impurities from solvent. Even though these minor impurities are present in the NMR, they do not seem to have affected the end-capping or the polymerization. Based on NMR analysis, the allyl end-capping worked, which is evident by the presence of allylic peaks. The yield of polymer chains that contain an allyl functionalized end-group is further confirmed with the MALDI-TOF analysis.

The MALDI-TOF spectrum shows the relative intensity of polymer chains with specific end-groups. After the magnesium-halogen exchange on the allyl-terminated poly(3-hexylthiophene), the intensity of the peaks corresponding to the polymer chains with bromine end groups (i.e. Br/H and Br/Allyl) were reduced. Furthermore, the peaks corresponding to the polymer chains with end-groups H/H and H/Allyl increased in intensity relative to the polymer chains containing bromine end groups. Thus, the magnesium-halogen exchange reaction was successful.

The magnesium-halogen exchange reaction was required to prevent any side reactions during the anionic coupling from the polyisoprene-*block*-polystyrenyl anion to the allyl functional group. Initially, the coupling reaction appeared successful due to the intense red color of the hexane fraction collected with the Soxhlet extraction. After the polymer was washed with cold cyclohexane, the NMR of the purified polymer illustrated the presence of each block in the polymer sample.

To illustrate that the material was a block copolymer a size exclusion chromatography analysis was performed. From the size exclusion chromatography, we can see that the addition of

each block decreased the molecular weight of the material. However, the molecular weight is still larger than that of the poly(3-hexylthiophene) homopolymer. The size exclusion chromatography analysis was relative to polystyrene homopolymer standards. Thus, the decreased molecular weight can be contributed to a shift in hydrodynamic volume with the growing blocks. This observable shift in hydrodynamic volume is confirmed with a different relative molecular weight for the purified triblock copolymer in a different solvent. Overall, the molecular weight of the polyisoprene-*b*-polystyrene-*b*-poly(3-hexylthiophene) cannot be confidently determined with this analytical technique. However, from the size exclusion chromatography trace of the polyisoprene-*b*-polystyrene-*b*-poly(3-hexylthiophene), the monomodality confirms that the material is not a blend (see Appendix A).

The mobility of charge carriers was determined by using organic field effect transistors with a bottom-gate bottom-contact configuration. Compared to the literature value of poly(3-hexylthiophene) homopolymer of similar molecular weight, the carrier transport of the polyisoprene-*b*-polystyrene-*b*-poly(3-hexylthiophene) is lower by four orders of magnitude. Furthermore, the threshold voltage was found to be 220 V, which is a large potential that is necessary to turn on the device. Furthermore, the on-off current ratio was calculated to be around to be 2.6 which parallels the results of the low mobility illustrating the materials poor performance on these devices. Although, there is not any morphological data to describe the material's phase separation behavior, the mobility data illustrates that there are not any systematic channels that elicits charge carrier hopping mechanisms. Furthermore, the low mobility is expected since 91% of the material contains insulating polymer.

Although the mobility of the triblock copolymer was poor, the material was successfully extruded with a custom pneumatic extrusion system. The triblock copolymer was readily extruded on the millimeter scale into simple two-dimensional and three-dimensional architectures without creeping or collapsing on itself. An important observation to note is that the material was extruded without the application of heat, which is unique among materials used for extrusion methods.

To improve the usefulness of the triblock copolymer, there needs to be an enhancement on the electronic properties which could be achieved in two ways. One way to improve the mobility is to incorporate more poly(3-hexylthiophene) which could be accomplished through a synthetic or a blending approach. Another way to improve the electronic properties would be to explore more advanced polymer systems that are self-doping or maintain conductivities for long periods of time. Furthermore, there needs to be a study on the mechanical properties of elastomeric block copolymers that incorporate poly(3-hexylthiophene), wherein the effect of increasing the composition of the poly(3-hexylthiophene) on the extrusion process needs to be addressed. On the other hand, the polyisoprene-*b*-polystyrene-*b*-poly(3-hexylthiophene) triblock copolymer was readily extruded at room temperature, which should not be expected when the elastomeric block is changed from polyisoprene. Therefore, an engineering requirement that involves a heating element is needed to extrude materials at the polymer's melting temperature.

CHAPTER 5

CONCLUSION

In conclusion, the polyisoprene-*b*-polystyrene-*b*-poly(3-hexylthiophene) block copolymer was successfully synthesized through anionic coupling. Furthermore, the material was readily extruded with a custom pneumatic extrusion system into two- and three-dimensional architectures at room temperature without any modifications to the polymer. However, due to a small mole percent composition of the poly(3-hexylthiophene) block, the electronic properties of the material fell short of what could be useful for flexible electronics. The composition of poly(3-hexylthiophene) will need to be increased for the material to be useful for flexible electronic applications. However, increasing the poly(3-hexylthiophene) content or changing the elastomeric segment may have effects on the printability of the material. Therefore, with some engineering to bring the polymers to melt, the elastomeric block copolymers that contain poly(3-hexylthiophene) have potential for three-dimensional printing applications.

APPENDIX

A. SEC Trace of purified Polyisoprene-*b*-Polystyrene-*b*-Poly(3-hexylthiophene)

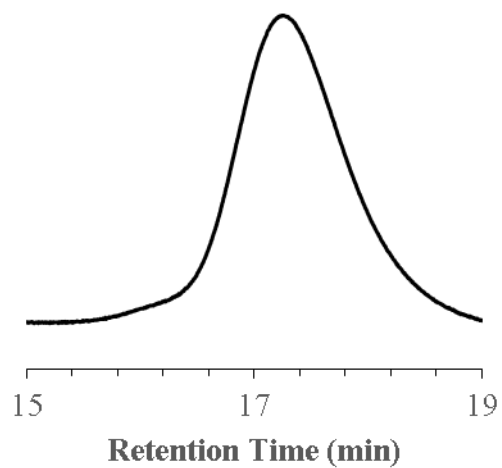


Figure A1. Size exclusion chromatography trace of the purified polyisoprene-*b*-polystyrene-*b*-poly(3-hexylthiophene) illustrating the monomodality of the peak.

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BIOGRAPHICAL SKETCH

Crystal Niermann is from Houston, Texas. After graduating high school in 2010, she attended Sam Houston State University. While at SHSU, Crystal participated in numerous undergraduate research opportunities. Briefly, Crystal studied the biosocial psychology of criminals in the Criminal Justice Department. After working in the Criminal Justice Department, Crystal worked in the Biology Department to study the neuroethology of grasshopper mice. She also participated in undergraduate research in the Chemistry Department where she studied the enzyme kinetics of P450. She graduated from SHSU in 2014 Magna Cum Laude with her ACS Certified Bachelor of Science in Chemistry. Crystal continued her education at The University of Texas at Dallas in the Chemistry Department, where she currently studies the extrusion of elastomeric semiconducting block copolymers for which she was recognized by ACS POLY Division for outstanding research with a Poster Award.

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Assigned to General Chemistry for Non-Science majors, General Chemistry for Science majors, Organic Chemistry, Quantitative Analysis, and Physical Chemistry 1. Prepared and executed lectures for a successful laboratory environment. Enforced laboratory safety. Graded lab reports.

Teaching Assistant

The University of Texas at Dallas

Assigned to General Chemistry and Quantitative Analysis. Assisted professors with laboratory lecture preparation materials, laboratory safety, and grading lab reports.

Research Assistant

The University of Texas at Dallas

Responsible for performing organic syntheses to produce semiconducting elastomeric polymer materials. I characterized the synthesized organic and polymer substances using GPC, MALDI-TOF, GC-MS, UV-VIS, FT-IR, DSC, TGA, and NMR. To characterize the performance of polymer materials I was responsible for fabricating and testing organic field effect transistors. Outside of research requirements, I maintained laboratory instruments (GC-MS, GPC, and UV-VIS) and glovebox. As designated safety officer, I enforced laboratory safety standards. Furthermore, I managed and coordinated group meetings, schedules, and laboratory roles.

CONFERENCE PRESENTATIONS

The influence of pain resistance on prey choice behavior in Grasshopper mice

Poster Presentation

International Society for Neuroethology Congress

Fall 2012

Super-Size Me: Studying the Prey Choice Behavior of Grasshopper Mice

Poster Presentation

Society of Integrated and Comparative Biology Annual Meeting

Spring 2013

3D Printing Semiconducting Elastomers

Oral Presentation

Texas Soft Matter Conference

Fall 2016

Semiconducting Elastomeric Block Copolymer containing Poly(3-hexylthiophene)

Poster Presentation/ Selected for Sci-Mix

ACS 252 National Meeting in Philadelphia, PA

Fall 2016

AWARDS AND HONORS

Outstanding Mentor Award

Young Women in Science and Engineering Investigator Program

Spring 2016

POLY Outstanding Poster Award

ACS 252 National Meeting in Philadelphia, PA

Fall 2016

Eric Moore Chemistry Graduate Student Scholarship

The University of Texas at Dallas

Department of Chemistry and Biochemistry

Fall 2016

PROFESSIONAL MEMBERSHIPS

American Chemical Society

Joined Fall 2013

Ongoing