Semiconducting Elastomeric Block Copolymers containing Poly(3-hexylthiophene)

Crystal Niermann*, Alex Haring‡, Tamer Elashyi*, Blake Johnson‡, Mihaela Stefan*
*Department of Chemistry, University of Texas at Dallas, Richardson, TX 75080
‡ Grado Department of Industrial and Systems Engineering, Virgina Tech, Blacksburg, VA

Email for Questions/Comments:
cxn141630@utdallas.edu

Introduction

Recently, there has been increased interest in flexible electronics because the technology offers ubiquitous application to the public and industry.[1] Furthermore, being able to print a three-dimensional conductive network provides a faster and cheaper means to prototype an electronic device.[2]

Generally, flexible electronic devices are fabricated with a conducting material dispersed within an elastic matrix. Poly(3-hexylthiophene), (P3HT), is a semiconducting polymer known for its facile processability and solubility in organic solvents. Furthermore, P3HT has successfully been integrated into electronic devices such as field effect transistors (**Figure 1**) and photovoltaics.[3] In order to obtain flexibility while maintaining conductivity, P3HT can be conjugated to an elastomeric polymer such as polyisoprene or polydimethylsiloxane.

Semiconducting elastic block copolymers can be synthesized through a variety of methods (e.g. radical, anionic, etc.). The material described below will be synthesized via anionic coupling mechanisms which provides all of the advantages of anionic polymerization while being able to efficiently produce a block copolymer.[4]

The three-dimensional printing properties of an elastomeric semiconducting block copolymer containing P3HT has been explored and is presented .

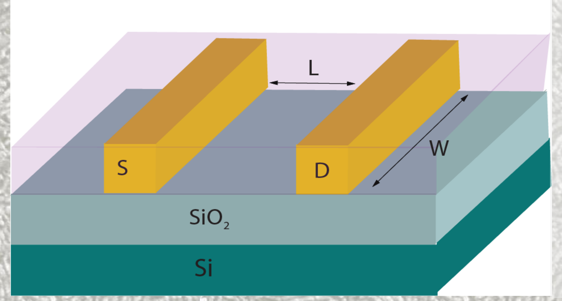


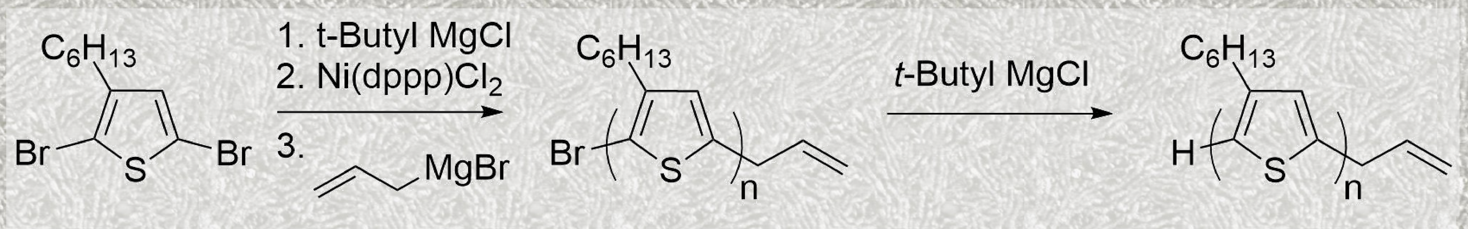
Figure 1. General schematic of a bottom-gate bottom-contact organic field effect transistor used to measure the mobility of semiconductors.

Experimental

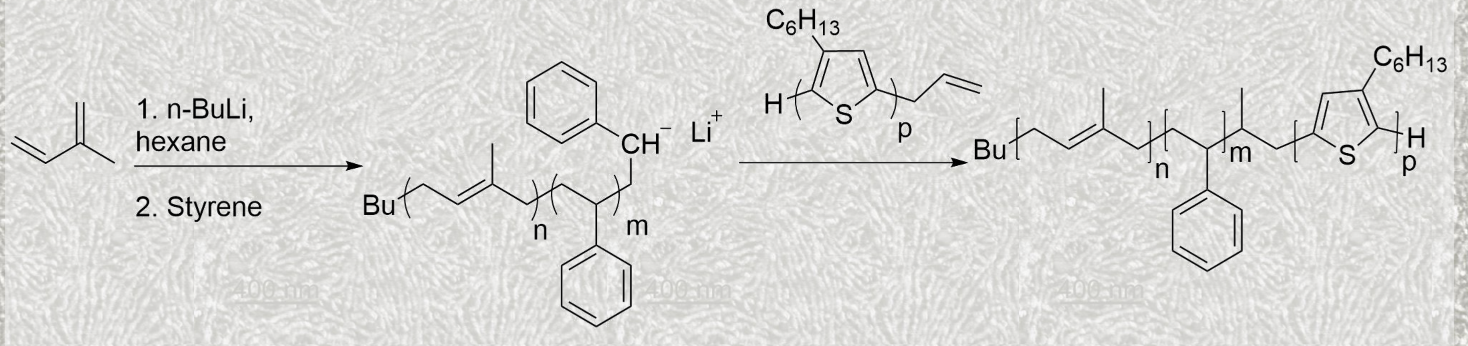
Allyl-terminated P3HT was synthesized via Grignard metathesis polymerization (GRIM). To prevent any side reactions, a magnesium-halogen exchange was performed on the allyl-terminated P3HT with excess Grignard reagent (**Scheme 1**).

An elastomeric semiconducting block copolymer was synthesized via anionic coupling of allyl-terminated P3HT to polystyrenyl anion (**Scheme 2**). The resulting triblock copolymer was extracted via Soxhlet extractions - methanol, hexane, followed by chloroform. The material that was extracted with hexane was washed with cold cyclohexane to remove excess homopolymer. The extracted material was analyzed with NMR and SEC.

To test for the electronic properties of the material, the block copolymer was tested on bottom-gate bottom-contact organic field effect transistors.



Scheme 1. Synthesis of allyl-terminated P3HT



Scheme 2. Synthesis of polyisoprene-*b*-polystyrene-*b*-P3HT

Results and Discussion

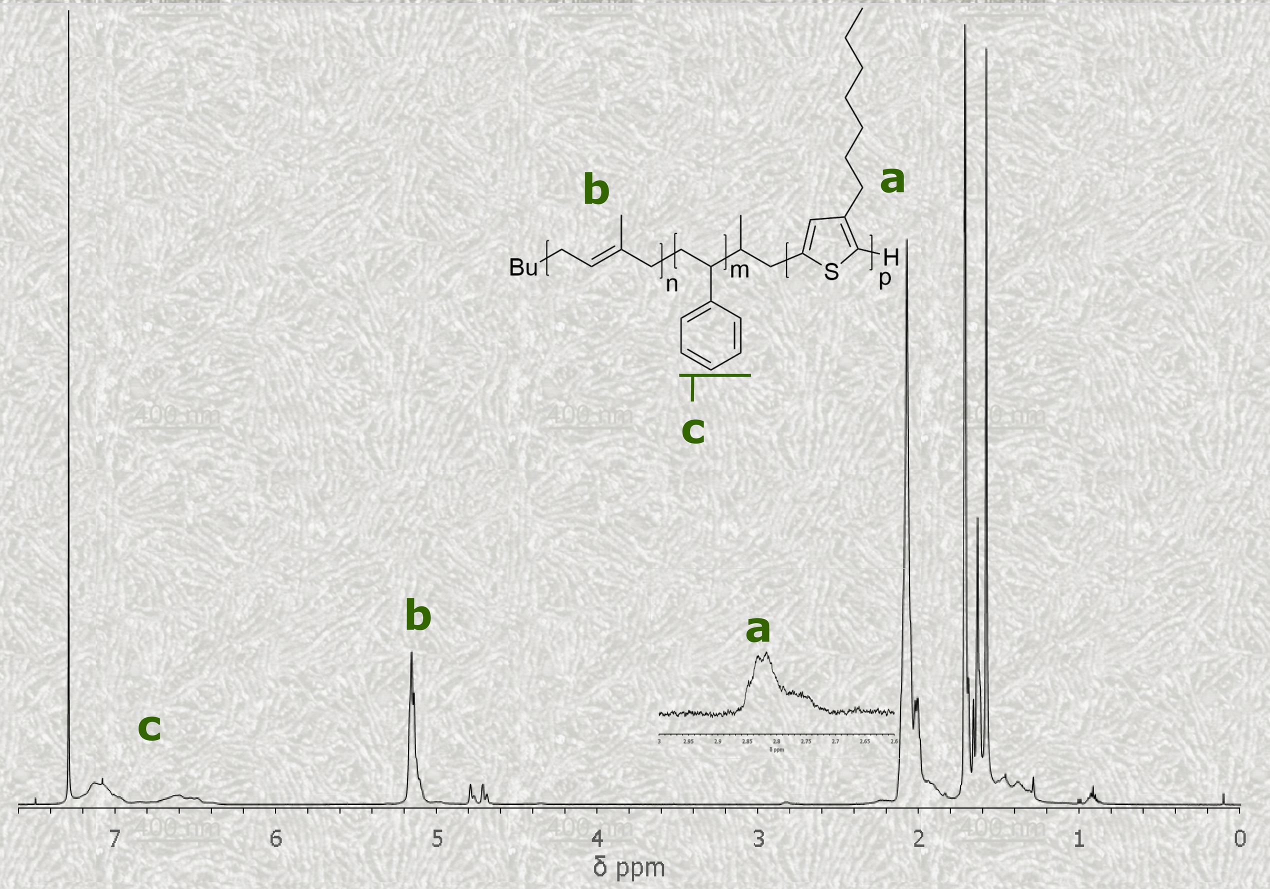


Figure 1. ^{1}H NMR spectrum polyisoprene-*b*-polystyrene-*b*-poly(3-hexylthiophene)

Table 1. Size Exclusion Chromatography
Solvent Line: THF *Calibration*: Polystyrene

Sample	M_n	PDI
Allyl-terminated P3HT	8,293	1.295
Polyisoprene	12,627	1.217
Polyisoprene-*b*-polystyrene	11,702	1.247
Hexane Fraction	10,084	1.215

Table 2. Mobility Analysis with Thin Film Transistors

Sample	Turn on Voltage (V)	I_{ON}/I_{OFF}	Average Mobility (cm^2/Vs)
P3HT homopolymer	13.5	10^3	1.24×10^{-3}
Triblock copolymer	242.1	2.3	5.53×10^{-6}

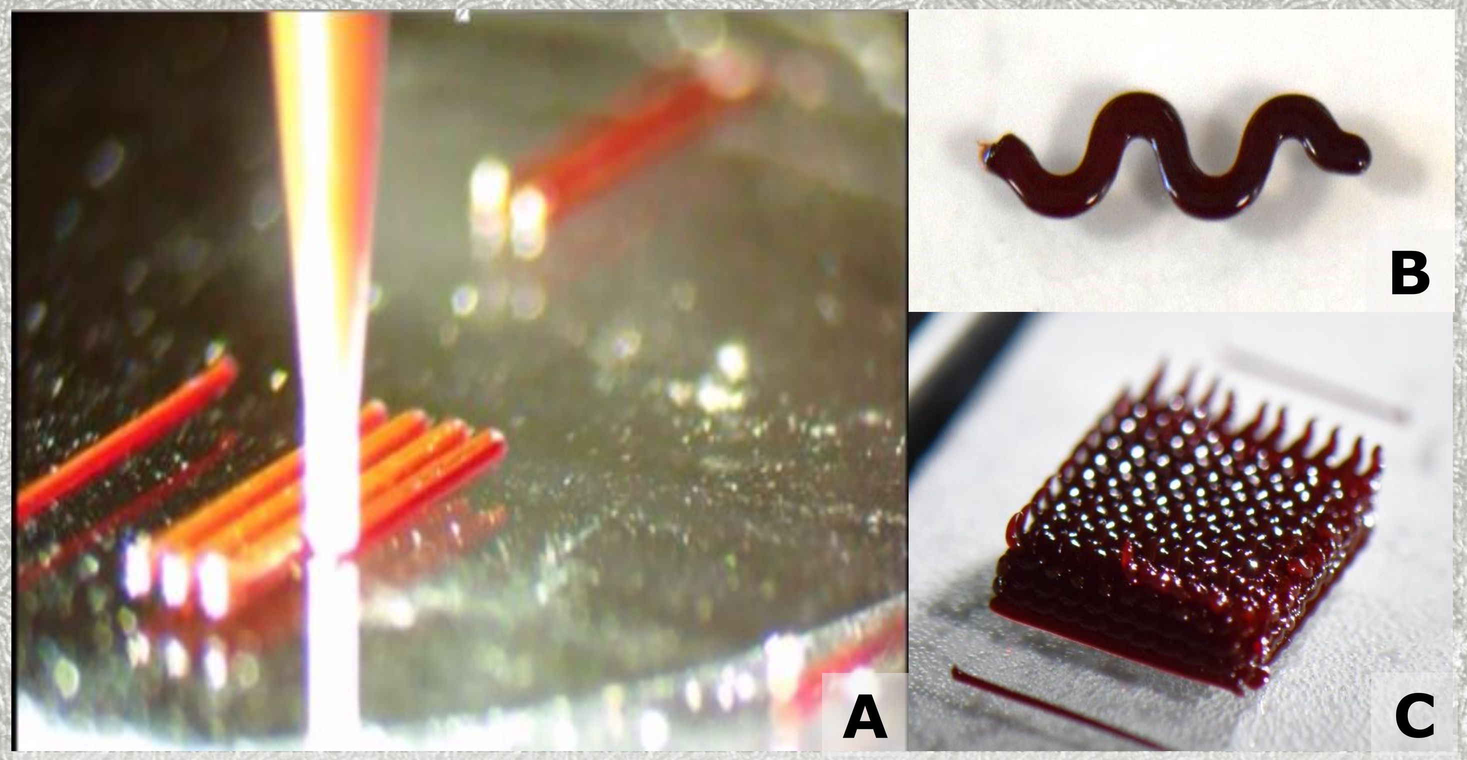


Figure 3. A) An image of the synthesized triblock copolymer being printed as a 2D linear array through a 27 G (210 µm) syringe tip at room temperature. B) An image of the triblock material printed in a 2D sigmoidal shape with dimensions of 5 x 1 mm. C) An image of the triblock material 3D printed as a grid with dimensions 5 x 5 x 3 mm.

Conclusion and Future Work

Based on NMR and SEC analysis (**Figure 1** and **Table 1**), the triblock copolymer was successfully synthesized via anionic coupling.

However, due to the low composition of P3HT in the extracted material, the mobility data is poor in comparison to standard organic semiconducting material (**Table 2**). Our current focus to better the electronic properties of this type of material is to increase the molecular weight of the P3HT block and/or to create polymeric blends.

We are also working towards 3D printing more crystalline material like that of polystyrene-*b*-P3HT. Furthermore, we are working towards using a variety of elastomeric blocks (e.g. polydimethylsiloxane and polymyrcene).

References

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