

Thiophene Based Donor/Acceptor Conjugated Polymers for Organic Photovoltaics

Brian Doyle, Rutgers University, SURF Fellow 2010

Faculty Advisor: Dr Seth Marder

Postdoc Mentors: Dr. Raghunath Dasari and Dr. Tissa Sajoto

Introduction

Over the last two decades, research in solar cells has grown rapidly as a response to the public need for a renewable and environmentally conscious energy resource. One emerging area of solar research focuses on synthesizing donor/acceptor conjugated copolymers to be paired with PCBM in a Bulk Heterojunction structure. These organic photovoltaics have the advantages of large scale processing, the ability to deposit on flexible substrates, and tunable electrochemical properties. However, cutting edge polymer solar cells currently peak at ~7% efficiency, which will need to increase to >10% in order for the production costs to compete with current market inorganic solar cells.

When designing these organic solar cells, there are four important characteristics to consider: ① low HOMO level for a higher V_{oc} , ② low band gap to maximize light absorption ③ planar structure for high hole mobility ④ solubility for large scale processing^[1]. The purpose of this research is to explore three copolymer combinations of a thiophene based donor and an electron deficient acceptor that display those characteristics. The monomer 4,4'-bis(alkyl)-5,5'-bis(trimethyltin)-dithienosilole is chosen as the donor due to its excellent electron mobility and efficient charge transfer that occurs because of bonding of the silicon atom with the butadiene moiety^[2]. The alkyl groups are added to improve solubility and complete the overall planar structure. This bithiophene monomer is polymerized with three previously synthesized electron deficient monomers with the goal of comparing the effects of different strength electron accepting groups on electrochemical properties and application to organic photovoltaics.

Synthesis

The monomer 4,4'-bis(alkyl)-5,5'-bis(trimethyltin)-dithienosilole was synthesized successfully from commercially available 2-bromothiophene, which was reacted with lithiumdiisopropylamide and quenched with trimethylsilane to obtain 2-bromo-5-silylthiophene. This compound was further reacted with LDA and $CuCl_2$ under a halogen-dance reaction pathway to yield key intermediate, (3,3'-dibromo-[2,2'-bithiophene]-5,5'-diyl)bis(trimethylsilane). The cyclized silole compound was obtained after reaction on the previous compound with $n-BuLi$ and di- n -alkylsilane in good yields. The TMS protected groups on the silole compound was replaced quickly with NBS via electrophilic substitution, after which it was converted into the distannyl derivative by lithiation and subsequently quenched with trimethyltin chloride.

The Stille coupling for the polymerization was accomplished through use of 1:1 equivalents of distannyl silole donor monomer and respective dibromide acceptor monomers in the

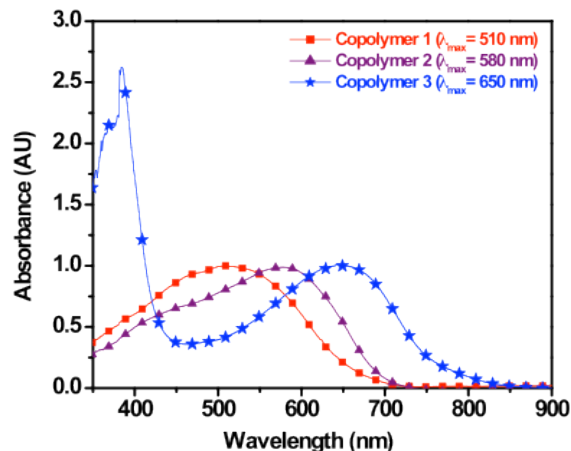


Figure 1. Absorption spectra for the three copolymers

presence of a 0.04 equivalent palladium catalyst in *o*-xylene solvent. The synthesis of copolymer 1 was performed through microwave heating conditions at 140°C for 10, 20, and 30 minutes; similarly, copolymer 2 was obtained via microwave heating at 150°C for 20, 30 and 40 minutes; and the copolymer 3 reaction conditions were 140°C for 20, 30, and 60 minutes. Each copolymer solution was then precipitated out in methanol and filtered out to obtain crude polymers.

Results and Discussion

The molecular weights of all three copolymers were estimated using Gel permeation chromatography with THF as eluent and their absorption spectral features in THF were obtained with UV-Vis spectroscopy (as shown in Figure 1). The Copolymer 1 showed low average molecular weights, M_n between 5.7 and 7.0 kDa and M_w between 5 and 11 kDa, which indicates a lower degree of polymerization. This copolymer showed a broad absorption peak with a peak maximum at 510 nm. The Copolymer 2 showed higher molecular weights, M_n between 7.5-10.0 kDa and M_w between 17.0-34.0 kDa, indicating greater degree of polymerization and showed a red shifted absorption in its UV-Vis spectrum. The copolymer 3 showed the highest molecular weights, M_n range of 25-28 kDa and M_w range of 86-117 kDa, and also showed the greatest shift toward the infrared part of the visible spectrum.

The data indicates a relationship that increasing the molecular weight and introducing a stronger electron accepting monomer results in a shift in the absorption spectra toward the infrared region. A smaller band gap would explain the shift toward the infrared, which could be caused by the higher molecular weight and stronger electron accepting monomer.

References

- [1] *Macromolecules*, **2010**, 43, 4609-4612
- [2] *Chemical Reviews*, **2009**, Vol. 109, No.11