

# Poly(3-alkyldithienothiophene): Synthesis, Structure and Optical Properties

Yuki Hamasaki

Applied Chemistry, Kyushu University, Fukuoka, Japan

NNIN iREG Site: NanoTech User Facility, University of Washington, Seattle, WA

NNIN iREG Principal Investigator: Prof. Christine K. Luscombe, Materials Science and Engineering, University of Washington

NNIN iREG Mentor: Dr. Ken Okamoto, Department of Materials Science and Engineering, University of Washington

Contact: y.hamasaki@mail.cstm.kyushu-u.ac.jp, luscombe@uw.edu, keno2@uw.edu

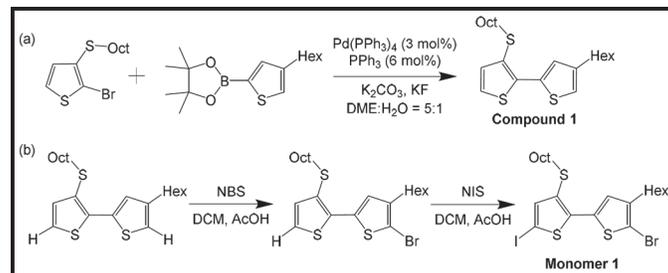
## Abstract:

Organic semiconductors that consist of conjugated oligomers or polymers are the subject of considerable current research interest, owing to their fundamental optoelectronic properties and their potential applications for organic photovoltaics. In this context the regioregular alternative copolymer of 3-alkylsulfanylthiophene (AST) and 3-alkylthiophene (AT), *alt*-P3AST-*co*-3AT, has an intriguing structure because the repeating unit can be transformed into 3-alkyldithienothiophene (3ADTT) to serve as a quinoid moiety. The preparation methods of *alt*-P3AST-*co*-3AT are discussed.

## Introduction:

Organic electronics is a growing area of research that investigates the properties and applications of conjugated polymers and semiconducting small molecules. Devices made from organic materials have the potential to be flexible, are inexpensive to process, and weigh less than their inorganic counterparts. Organic photovoltaic (OPV) devices are currently under investigation as a low-cost alternative to silicon-based photovoltaic devices. Poly(3-hexylthiophene) (P3HT) is one of the most successful homopolymers due to its semi-crystalline structure, strong light absorption properties, and high charge carrier mobility [1]. However, the short-circuit current density ( $J_{sc}$ ) and open-circuit voltage ( $V_{oc}$ ) of P3HT devices are limited due to a wide HOMO-LUMO gap and high HOMO energy level. For these reasons, quinoid polymers are being developed to control the energy levels. Since the quinoid resonance form is lower in energy than the aromatic form, stabilizing the quinoid form will effectively reduce the band gap of related conjugated polymers. According to a theoretical calculation using the Semi-empirical Method, AM1, dihedral angles of regioregular 3-ethylthiophene and 3-thioalkylthiophene, 3-hexyldithienothiophene are 143.8° and 179.5°, 179.7°, respectively.

Here, we report another approach to the design and synthesis of new organic semiconductors for photovoltaics, using the fused thiophene derivative, dithieno[3,2-b:2',3'-d]thiophene as a building block.



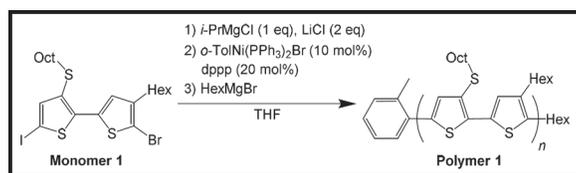
Scheme 1: Monomer synthesis.

## Experimental Procedure:

### Synthesis of 5-bromo-4-hexyl-5'-iode-3'-(octylsulfanyl)-2,2'-bithiophene (Monomer 1) via Suzuki coupling method (Scheme 1)

(a) **4-hexyl-3'-(octylsulfanyl)-2,2'-bithiophene (Compound 1).** Compound 1 was prepared via Suzuki coupling [2]. In N<sub>2</sub>, 2-bromo-3-(octylsulfanyl)thiophene (5 mmol), 4-hexylthiophene-2-boronic acid (7 mmol), K<sub>2</sub>CO<sub>3</sub> (12.5 mmol, 1.73 g), 10 mL DME and 2 mL distilled water were added to a Schlenk flask. After degas-stirring for 30 minutes, triphenylphosphine (PPh<sub>3</sub>) (77.5 mg, 0.3 mmol), Pd(PPh<sub>3</sub>)<sub>4</sub> (0.173 g, 0.15 mmol) and KF (12.5 mmol, 0.725 g) were added. The mixture was allowed to stir under 90°C (oil bath) overnight. After quenching with NH<sub>4</sub>Cl, the reaction mixture was extracted with ethyl acetate. The solvent was evaporated under vacuum. Flash chromatography on silica gel (hexane) gave the Compound 1.

(b) **5-bromo-4-hexyl-5'-iode-3'-(octylsulfanyl)-2,2'-bithiophene (Monomer 1).** 4-hexyl-3'-(octylsulfanyl)-2,2'-bithiophene (3.21 mmol, 1.27 g) was added to a flask with 5 mL acetic acid and 5 mL DCM stirring at 0°C. To the flask was added NBS (3.21 mmol, 0.572 g). The solution was brought to room temperature and allowed to stir for one hour before being poured into 50 mL of 10% Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>, and then extracted with diethyl ether. The organic phase was finally dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, and evaporated under vacuum to yield a crude oil. Flash chromatography on silica gel (hexanes) gave



Scheme 2: Polymerization.

the 5-bromo-4-hexyl-3'-(octylsulfanyl)-2,2'-bithiophene. Then, 5-Bromo-4-hexyl-3'-(octylsulfanyl)-2,2'-bithiophene (0.861 mmol, 0.409 g) was added to a flask with 2 mL acetic acid and 2 mL DCM stirring at 0°C. To the flask was added NIS (0.861 mmol, 0.194 g). The solution was brought to room temperature and allowed to stir for 30 minutes before being poured into Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>, and then extracted with diethyl ether. The organic phase was finally dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, and evaporated under vacuum to yield a crude oil. Flash chromatography on silica gel (hexanes) gave the Monomer 1.

**Initiated Polymerization (Scheme 2).** In a procedure adapted from literature [3], Monomer 1 (0.178 g, 0.297 mmol) and 44.5 mg lithium chloride was dissolved in THF (10 mL) and cooled to 0°C with stirring. Then 0.15 mL of a 2.0 M isopropyl magnesium chloride in hexanes was added dropwise over 5 min and stirring continued for 30 minutes. At this point, a solution consisted of 22.3 mg of *cis*-chloro(*o*-tolyl)1,3-bis(diphenylphosphino)propanenickel(II) (10 mol%) and 24.5 mg of diphenylphosphinopropane (dppp) (20 mol%) was added rapidly via syringe. The reaction was allowed to warm to room temperature. The solution was left to polymerize over 10 hours, then quenched with a solution consisted of hexylbromide (0.178 mL, 2 mmol) and magnesium (54.5 mg, 2.2 mmol) in diethyl ether. The reaction mixture was washed by MeOH, acetone, and hexane, in order.

## Results and Future Works:

We have succeeded in synthesizing 5-bromo-4-hexyl-5'-iodo-3'-(octylsulfanyl)-2,2'-bithiophene, which evaluated by <sup>1</sup>H NMR (Figure 1). Polymer 1 showed too complex a NMR spectrum to assign. The next step will be chemical transformation of *ot*-P3OST-*co*-3HT to P3HDTT and measuring the optical

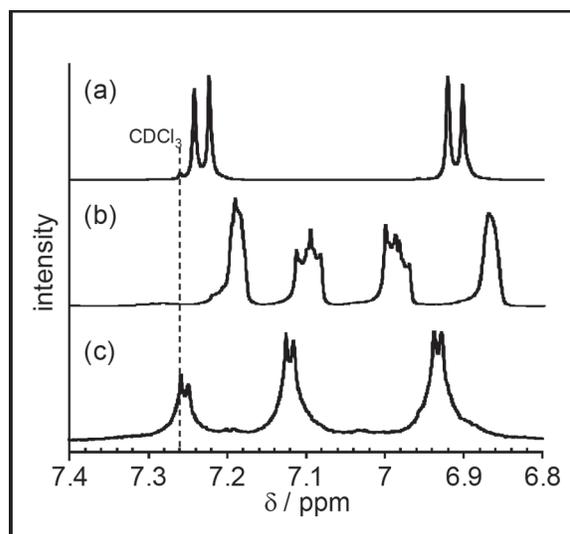


Figure 1: NMR spectra of 2-bromo-3-(octylsulfanyl)thiophene (a), Compound 1 (b), and Monomer 1 (c).

properties of synthesized polymer. Moreover, we will fabricate the OPV device consisted of P3HDTT and evaluate their properties.

## Acknowledgments:

This research was supported by the National Nanotechnology Infrastructure Network (NNIN), the National Science Foundation (NSF) and National Institute for Material Science (NIMS). I would also like to thank the Luscombe Lab for their valuable guidance and assistance, and the NanoTech User Facility (NTUF) at the University of Washington for providing the equipment and training necessary for this project.

## References:

- [1] Youngkyoo Kim, Jenny Nelson, Donal D. C. Bradley et al., *Nature Mater.* 2006, 5, 197-203.
- [2] Dong, C.-G., T.-P. Liu, and Q.-S. Hu, *SYNLETT* 2009, 1081-1086.
- [3] Hugo A. Bronstein, Christine K. Luscombe, *J. Am. Chem. Soc.* 2009, 131, 12894-12895.