

# COMPARATIVE STUDY OF POLY(3-ALKYLTHIOPHENE) TRI-BLOCK COPOLYMERS

Jessica R. Cooper, Rui Zhang, Mihaela C. Iovu  
Richard D. McCullough, \* Tomasz Kowalewski

Department of Chemistry, Carnegie Mellon University, 4400 Fifth Avenue,  
Pittsburgh, Pennsylvania

## Introduction

Due to its chemical structure, regioregular poly(3-alkylthiophene) (PAT) possesses an array of desired electrical properties<sup>4,5</sup>. However, its chemical structure also causes PAT to form brittle and highly inflexible rod like microstructures. The objective is to produce a material that has the electrical properties of polythiophene and the flexibility of soft polymers such as poly(methyl acrylate)<sup>7</sup>, poly(methyl methacrylate), or polystyrene.

This work is focused on the synthesis and characterization of a variety ABA triblock copolymers, where the A block can be poly(methyl methacrylate), poly(styrene), or poly(methyl acrylate) and the B block is regioregular poly(3-hexylthiophene). Regioregular poly(3-hexylthiophene) (PHT) was synthesized by using Grignard Metathesis reaction<sup>6</sup>. End group modification of regioregular polythiophene leads to the production of a macroinitiator<sup>8</sup>. Atom Transfer Radical Polymerization (ATRP)<sup>9,10,11</sup> then is utilized to produce triblock copolymers using the PHT macroinitiator as the precursor. The morphology and electrical properties of the three different block copolymers will be compared and analyzed.

## Experimental

**Materials.** All reactions were performed under pre-purified nitrogen, using either flame-dried or oven-dried glassware. All solvents were distilled prior to use. LiAlH<sub>4</sub> and Grignard reagents were purchased from Aldrich Chemical Co. and used without further purification. N-methylformanilide, POCl<sub>3</sub>, triethylamine, and 2-bromopropionyl bromide were distilled prior to use.

**Instrumentation.** <sup>1</sup>H spectra were recorded on an IBM Bruker FT500 MHz spectrometer. All NMR spectra were recorded in CDCl<sub>3</sub> containing 0.003% TMS as an internal standard. MALDI-TOF MS was performed using a Voyager-DE STR BioSpectrometry Workstation by PerSeptive Biosystems. All GPC spectra were recorded using a Waters 6000A apparatus and a Waters R410 differential refractometer. The eluent was THF, which was kept at 25°C. Flow rate was 1.0 mL/min. The system was calibrated using polystyrene standards obtained from Polymer Standards Service. GC/MS was performed on a Hewlett-Packard Agilent 6890-5973 GC-MS workstation.

**Synthesis of poly(3-hexylthiophene) with H/H end groups.** Regioregular poly(3-hexylthiophene) (1.0 g, 0.1 mmol) was dissolved in THF (150 mL). Alkyl grignard reagent (2M, 10 mL) was added and the mixture was refluxed for 2 hours. The polymer was then precipitated in methanol.

**Synthesis of poly(3-hexylthiophene) with CHO/CHO end groups.** Poly(3-hexylthiophene) with H/H end groups (0.9g, 0.09 mmol) was dissolved in toluene (200 mL). N-methylformanilide (2 mL, 16 mmol) and POCl<sub>3</sub> (1.3 mL, 14 mmol) were added, and the mixture was stirred at 75°C for 24 hours. The solution was cooled to room temperature and then stirred with saturated sodium acetate. The polymer was precipitated in methanol.

**Synthesis of poly(3-hexylthiophene) with CH<sub>2</sub>OH/CH<sub>2</sub>OH end groups.** Poly(3-hexylthiophene) with CHO/CHO end groups (0.8 g, 0.08 mmol) was dissolved in THF (200 mL). LiAlH<sub>4</sub> (1M, 1 mL) was added to the solution. The mixture was allowed to stir at room temperature for 1 hour and then precipitated in methanol.

**Synthesis of poly(3-hexylthiophene) with bromoester end groups.** Poly(3-hexylthiophene) with CH<sub>2</sub>OH/CH<sub>2</sub>OH end groups (0.7 g, 0.07 mmol) was dissolved in THF (200mL). The solution was heated to 50°C followed by the addition of triethylamine (3 mL, 20 mmol) and drop-wise addition of 2-bromopropionyl bromide (2.5 mL, 20 mmol). The solution was allowed to stir at room temperature for 12 hours and then precipitated in methanol.

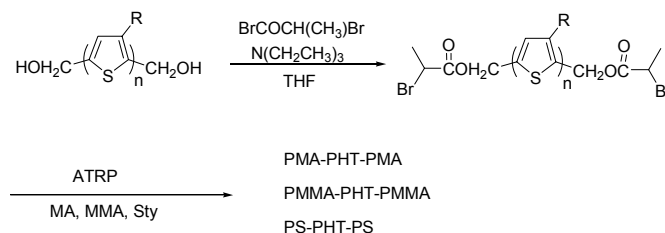
**ATRP of methyl acrylate (MA) using PHT macroinitiator (PHT-MI).** ATRP of methyl acrylate was performed at molar ratio: [MA] : [PHT-MI] : [CuBr] : [PMDETA] = 500 : 1 : 3 : 3, at 90°C.

## Results and Discussion

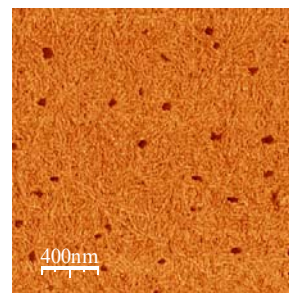
The ATRP macroinitiator is achieved through chemical modification of the end groups of regioregular poly(3-hexylthiophene) (PHT). The reaction sequence as described in literature by McCullough and coworkers<sup>7,8</sup> starts with a magnesium-halogen exchange converting a H/Br polymer to H/H terminated polymer. Through utilization of Vielsmier reaction, the polymer end groups are converted to aldehydes, which are then subsequently reduced to hydroxy groups. The hydroxy end groups were converted to bromoester end groups generating ATRP macroinitiator as shown in scheme 1.

Methyl acrylate, methyl methacrylate, and styrene were polymerized using the PHT macroinitiator as the precursor and CuBr-PMDETA as catalyst, yielding poly(methyl acrylate)-b-poly(3-hexylthiophene)-b-poly(methyl acrylate) (PMA-PHT-PMA), poly(methyl methacrylate)-b-poly(3-hexylthiophene)-b-poly(methyl methacrylate) (PMMA-PHT-PMMA), and polystyrene-b-poly(3-

hexylthiophene)-b-polystyrene (PS-PHT-PS) co-polymers respectively. The three triblock copolymers were characterized by the use of <sup>1</sup>H NMR spectroscopy and MALDI TOF-MS. The electrical properties and morphology of these triblock copolymers were also investigated. Figure 1 shows the nanostructure of PMA-PHT-PMA triblock copolymer.



**Scheme 1.** Reaction pathway for the synthesis of poly(methyl acrylate)-b-poly(3-hexylthiophene)-b-poly(methyl acrylate)



**Figure 1.** Tapping Mode AFM phase contact image of PMA-PHT-PMA.

## Conclusion

Poly(methyl acrylate)-b-poly(3-hexylthiophene)-b-poly(methyl acrylate), poly(methyl methacrylate)-b-poly(3-hexylthiophene)-b-poly(methyl methacrylate), and polystyrene-b-poly(3-hexylthiophene)-b-polystyrene were successfully synthesized using end group modification of poly(3-hexylthiophene) followed by atom transfer radical polymerization (ATRP) of monomer.

**Acknowledgements.** The authors of this paper would like to thank NSF, NIOSH, and MURI for financial support of this research. Special thanks to Dr. Roberto R. Gil for the NMR analysis

## References

- (1) Skotheim, T. A. *Handbook of Conducting Polymers*; Marcel Dekker: New York, **1986**.
- (2) (a) Heuer, H. W.; Wehrmann, R.; Kirchmeyer, S. *Adv. Funct. Mater.* **2002**, *12*, 89. (b) De Paoli, M. A.; Nogueira, A. F.; Machado, D. A.; Longo, C. *Electrochim. Acta*, **2001**, *46*, 4243. (c) Groenendall, L. B.; Zotti, G.; Aubert, P. H.; Waybright, S. M.; Reynolds, J. R. *Adv. Mater.* **2003**, *15*, 855.
- (3) Skotheim, T. A.; Reynolds, J. R.; Elsenbaumer, R. L. *Handbook of Conducting Polymers*; Marcel Dekker: New York, **1998**.
- (4) (a) McCullough, R. D.; Lowe, R. D.; Jayaraman, M.; Ewbank, P.C.; Anderson, D. L.; Tristram-Nagle, S. *Synth. Met.* **1993**, *55*, 1198. (b) McCullough, R. D.; Williams S. P.; Tristram-Nagle, S.; Jayaraman, M.; Ewbank, P. C.; Miller, L. *Synth. Met.* **1996**, *67*, 279.
- (5) Chen, T. A.; Wu, X.; Rieke, R. D. *J. Am. Chem. Soc.* **1995**, *117*, 233.
- (6) (a) Lowe, R. S.; Khersonsky, S. M.; McCullough, R. D. *Adv. Mater.* **1999**, *11*, 250. (b) Loewe, R. S.; Ewbank, P. C.; Liu, J.; Zhai, L.; McCullough, R. D. *Macromolecules* **2001**, *34*, 4324.
- (7) Liu, J.; Sheina, E.; Kowalewski, T.; McCullough, R. D. *Angew. Chem. Int. Ed.* **2002**, *41*, 329.
- (8) Liu, J.; McCullough, R. D. *Macromolecules*, **2002**, *35*, 9882.
- (9) Wang, J.-S.; Matyjaszewski, K. *J. Am. Chem. Soc.*, **1995**, *117*, 5614.
- (10) Matyjaszewski, K.; Xia, J. *Chem. Rev.* **2001**, *101*, 2921-2990.
- (11) Matyjaszewski, K.; Davis, T. P. Eds. *Handbook of radical polymerization*; Wiley-Interscience: Hoboken, 2002.